

THE JOURNAL OF GENERAL CHEMISTRY OF THE U.S.S.R.

Volume XXIV, No. 7

July, 1954

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

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259 West 14th Street

New York 11, N.Y.

Printed in the United States

Annual subscription \$95.00

Single issue 20.00

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ANHYDROUS METANIOBATES AND METATANTALATES OF THE ALKALI METALS

I. METANIOBATES OF THE ALKALI METALS

M. A. Pchelkina and A. V. Lapitsky

The literature contains information about the preparation of lithium metaniobate [1], sodium metaniobate [2], and potassium metaniobate [3]. There are no data for the preparation of rubidium and cesium metaniobates.

Our objective was the preparation of rubidium and cesium metaniobates and a study of some properties of the metaniobates of the alkali metals.

EXPERIMENTAL

Starting Substances

Niobium pentoxide. The starting raw material for preparation of pure niobium pentoxide was the technical mixture known as "tantalum-niobium residue" containing the two elements in approximately 1:1 ratio. The principle extraneous substances present were oxides of iron, tin and silicon. The titanium content was negligible. For the preparation of pure niobium pentoxide, a certain amount of "residue" was mixed with 3 times its weight of 10% Na_2CO_3 and 90% NaOH and sintered at 700° in a silver dish. After cooling, the sintered mass was extracted from the beaker, pulverized in a porcelain mortar, transferred to a beaker and treated with distilled water. During the leaching process the tin and silicon went into solution in the form of sodium stannate and silicate, while the sodium niobate and tantalate (insoluble in presence of excess of alkali) remained in the residue. After two decantations the residue was dissolved in a large quantity of hot water to form a cloudy solution. The latter was filtered, and the filtrate was evaporated down before treating twice with 10% acetic acid solution; this treatment brought down a white, voluminous precipitate of the hydrated pentoxides of niobium and tantalum. For removal of the iron oxide, the precipitate was washed with acetic acid solution followed by 5% ammonium carbonate solution.

Separation of the niobium from the tantalum was effected by dissolving the mixture in 40% hydrofluoric acid. To the resultant colorless, transparent solution was added a saturated solution of potassium fluoride prepared in the amount required for formation of the double fluorides.

The acidity of the solution was about 2%, which is the optimum for complete separation of the two elements [4]. The crystals of potassium fluorotantalate were separated from the solution by filtration through a lead funnel, and they were washed with cold distilled water for removal of sodium oxyfluoroniobate solution. The wash liquors were combined with the filtrate which contained the main bulk of potassium oxyfluoroniobate; the liquid was evaporated to dryness. The salt in the dish was heated to 120° and then dissolved in water by heating on a water bath. To the hot solution was added 0.5 ml hydrofluoric acid and 2 ml saturated potassium carbonate solution. A negligible amount of the salt, $\text{K}_4\text{Ta}_4\text{O}_{15}\text{F}_{14}$, came down after a short time and was filtered off. The above-described operation of tantalum separation was repeated but no precipitate was formed.

The solution of potassium oxyfluoroniobate was decomposed with concentrated ammonium hydroxide solution. The white precipitate of niobium pentoxide was washed first with dilute acetic acid solution and then with 5% ammonium carbonate solution.

Chemical analysis of the prepared niobium pentoxide, carried out by the known methods [5, 6, 7], showed that it was sufficiently pure and contained negligible amounts of impurities. A qualitative test for titanium [8] gave a negative result.

Spectrum analysis revealed an insignificant content of titanium, tantalum, iron and silicon. The lines of these elements were much less intense than the niobium lines.

Rubidium and cesium carbonates. We prepared these from chemically pure grades of the corresponding chlorides.

Weighed amounts of the starting salts were dissolved in the minimum amount of water. The resultant saturated solutions were treated with concentrated nitric acid while heating on a water bath. Excess of acid was taken. The end of the operation was indicated by the absence of chlorine in a check sample. The solutions of rubidium and cesium nitrates were treated with small portions of dry oxalic acid until oxides of nitrogen ceased to come off. The oxalates formed in this stage were heated in platinum dishes, gently at first and then strongly until completely converted into carbonates.

Preparation of Anhydrous Rubidium and Cesium Metaniobates.

Niobium pentoxide, previously calcined at 800° was thoroughly pulverized in an agate mortar and mixed with equimolar amounts of rubidium and cesium carbonates. The mixtures were transferred to platinum crucibles and heated at 800° for 4 hours. This period was required for completion of the reaction, as was indicated by the attainment of constant weight.

The prepared rubidium and cesium metaniobates were removed from their crucibles and treated with dilute hydrochloric acid for removal of any excess of the corresponding carbonate which had not reacted; the salts were then washed with water, dried, and calcined.

Both salts were analyzed for their content of niobium pentoxide and metallic oxide. A weighed amount of the salt was fused in porcelain crucibles with a tenfold amount of ammonium hydrosulfate. The transparent melts, after cooling, were treated with saturated ammonium carbonate solution. The contents of the beakers were heated on a water bath for an hour. The flocculent precipitates of niobium pentoxide were transferred to a filter and washed with 5% ammonium carbonate solution; after drying, the filters were ashed and the precipitates calcined to constant weight at 800°. The final weights gave the content of niobium pentoxide.

The filtrates contained, apart from rubidium (cesium) sulfate, considerable amounts of ammonium pyrosulfate and ammonium sulfate. The solutions were slowly evaporated to dryness on a water bath and then cautiously heated at a slightly higher temperature for removal of traces of water. After final dehydration, the sulfates were calcined; in this operation, as Spitsyn has shown [9], rubidium and cesium sulfates are fairly stable up to 800° whereas ammonium sulfate decomposes at a little above 350°. On attainment of constant weight, the rubidium and cesium were found in the form of sulfates.

Below are set forth the results of analyses of rubidium and cesium metaniobates.

Analysis of rubidium metaniobate.

Weights of samples 0.2008 and 0.2028 g.

Found %: Nb_2O_5 58.55, 58.86; Rb_2O 41.40, 41.32. RbNbO_3 . Calculated %: Nb_2O_5 58.85; Rb_2O 41.15.

Analysis of cesium metaniobate.

Weights of samples 0.2018 and 0.2036 g.

Found %: Nb_2O_5 48.72, 48.34; Cs_2O 50.95, 50.82. CsNbO_3 . Calculated %: Nb_2O_5 48.53; Cs 51.47.

The analytical data justify the conclusion that the prepared compounds are actually rubidium metaniobate and cesium metaniobate.

For the purpose of studying some of the properties of alkali metal metaniobates, we also prepared the metaniobates of lithium, sodium and potassium by the previously described methods [1, 10, 11]. Analytical results are set forth below.

Analysis of lithium metaniobate.

Weights of samples 0.2012 and 0.1930 g.

Found %: Nb_2O_5 90.10, 90.18; Li_2O 10.00, 9.96. LiNbO_3 . Calculated %: Nb_2O_5 89.90; Li_2O 10.10.

Analysis of sodium metaniobate.

Weights of samples 0.2010 and 0.1996 g.

Found %: Nb_2O_5 81.12, 81.20; Na_2O 19.12, 19.28. NaNbO_3 . Calculated %: Nb_2O_5 80.74; Na_2O 19.26.

Analysis of potassium metaniobate.

Weights of samples 0.2002 and 0.1973 g.

Found %: Nb_2O_5 74.20, 74.44; K_2O 25.98, 25.88. KNbO_3 . Calculated %: Nb_2O_5 73.89; K_2O 26.11.

Thermal Stability and Volatility of Metaniobates of the Alkali Metals

Lithium, sodium and potassium metaniobates have high melting points and are evidently thermally stable substances. We investigated the thermal stability and volatility of all the anhydrous metaniobates prepared in this research.

The volatility was determined in an open crucible furnace at a temperature of 1200°. The first experiments showed that none of the investigated salts was volatile when heated for 2 and 6 hours; continuous heating was therefore applied for 24 hours at the same temperature. As in the preceding experiments, no losses in weight were found.

It may be mentioned that the metaniobates of lithium, potassium and cesium were melted at 1200° and retained their color unchanged.

Due to the lack of volatility of these salts even on prolonged heating, we carried out experiments for determination of their volatility in vacuum.

Volatility determinations were carried out at 1200° and a pressure of about 1 mm. The data obtained show that even under these conditions none of the salts is volatile.

Lowering of the pressure does not affect the thermal stability of metaniobates of the alkali metals. The thermal stability of metaniobates of the alkali metals can probably be accounted for by the ionic bond and by the stability of the NbO_3^{-1} ion [12]. The oxygen atoms of this ion are firmly anchored to the central atom and evidently do not manifest a tendency to polarize the ions of the alkali elements. All the metaniobates of the alkali metals are sparingly soluble in water.

TABLE
Equivalent and Specific Electrical Conductivities of Saturated Aqueous Solutions of Metaniobates of the Alkali Metals at 25°

(Cell constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
LiNbO_3	$1.01 \cdot 10^{-4}$	$4.50 \cdot 10^{-5}$
NaNbO_3	$6.41 \cdot 10^{-5}$	$2.82 \cdot 10^{-5}$
RbNbO_3	$7.70 \cdot 10^{-5}$	$3.31 \cdot 10^{-5}$
CsNbO_3	$1.11 \cdot 10^{-4}$	$4.93 \cdot 10^{-5}$

We measured the equivalent and specific electrical conductivities of solutions saturated at 25°. The results are set forth in the Table

SUMMARY

1. Anhydrous metaniobates of rubidium and cesium were synthesized for the first time.

2. A study of the thermal stability of all the metaniobates of the alkali metals showed that all these salts are thermally stable at a temperature of 1200°.

3. Causes of the stability of the compounds in question were discussed.

4. Measurements were made of the equivalent and specific electrical conductivities of saturated solutions of metaniobates of the alkali metals.

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* T.p. = C.B. Translation pagination.

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ANHYDROUS METANIOBATES AND METATANTALATES OF THE ALKALI METALS

II. METATANTALATES OF THE ALKALI METALS

M. A. Pchelkina and A. V. Lapitsky

Very little information has been published about the anhydrous metatantalates of the alkali metals. Up to now only the metatantalates of sodium and potassium have been described [1]. We have synthesized the anhydrous metatantalates of the alkali metals and have studied some of their properties.

EXPERIMENTAL

Starting Substances

Tantalum pentoxide. Pure tantalum pentoxide was prepared from potassium fluorotantalate [2]. The crystalline precipitate (washed free from mother liquor) of sparingly soluble potassium fluorotantalate was recrystallized from 2% hydrofluoric acid solution, transferred to a lead dish and treated with concentrated sulfuric acid until completely decomposed. The slurry-like mass was washed into a large porcelain beaker, water was poured over it, and the tantalum pentoxide was thereby largely peptized by the sulfuric acid. To avoid the passage of the tantalum pentoxide into solution, the contents of the beaker were neutralized with ammonium hydroxide. The voluminous white precipitate of tantalum pentoxide was washed on the filter with 5% ammonium carbonate solution until disappearance of sulfate ion from the wash water. The tantalum pentoxide purified in this way was sufficiently pure.

Carbonates of alkali metals. The lithium carbonate was the chemically pure grade. The carbonates of rubidium and cesium used for preparation of tantalates have already been described by us [2].

Preparation of Anhydrous Metatantalates of Lithium, Rubidium and Cesium

After igniting at 800°, the pure tantalum pentoxide was finely pulverized and stirred with equimolar amounts of carbonates of lithium, rubidium and cesium. The prepared mixtures were placed in platinum crucibles (the mixture containing lithium carbonate was placed in a corundum crucible). Sintering was carried out in a crucible furnace at 800° for 4 hours. Attainment of constant weight was taken as the criterion of completion of the reaction. Even though we took a very small excess of the carbonate of the alkali metal, it was nevertheless necessary to remove its residues. It is known that reaction of tantalum pentoxide with excess of alkali metal carbonate can lead to formation also of soluble tantalates which pass into solution when the metatantalates are treated with water.

The metatantalates were treated with distilled water, washed with 2% acetic acid solution, dried, and ignited. Analyses, carried out for content of tantalum pentoxide and alkali metal oxide, determined as sulfate [2], showed that we had actually obtained the anhydrous metatantalates of lithium, rubidium and cesium. Below we set forth the results of the analyses of the prepared salts.

Analysis of lithium metatantalate.

Weights of substance 0.2020 and 0.2026 g.

Found %: Ta_2O_5 94.02, 93.98; Li_2O 5.84, 6.12. LiTaO_3 . Calculated %: Ta_2O_5 93.66; Li_2O 6.44.

Analysis of rubidium metatantalate.

Weights of substance 0.2028 and 0.1916 g.

Found %: Ta_2O_5 71.08, 71.12; Rb_2O 28.81, 28.88. RbTaO_3 . Calculated %: Ta_2O_5 70.83; Rb_2O 29.17.

Analysis of cesium metatantalate.

Weights of substance 0.1822 and 0.1618 g.

Found %: Ta_2O_5 60.82, 61.18; Cs_2O 39.04, 39.16. CsTaO_3 . Calculated %: Ta_2O_5 61.05; Cs_2O 38.94.

As in the case of metaniobates, we decided to investigate the thermal stability of the metatantalates of the alkali metals. For this purpose we prepared the anhydrous metatantalates of sodium and potassium by the method which has been frequently described [1].

The method used was entirely identical with that described for the synthesis of the metatantalates of lithium, rubidium and cesium. We analyzed the prepared metatantalates of sodium and potassium for their content of tantalum pentoxide and alkali metal oxide.

Analysis of sodium metatantalate.

Weights of substance 0.2010 and 0.2020 g.

Found %: Ta_2O_5 88.36, 88.57; Na_2O 11.01, 11.38. $NaTaO_3$. Calculated %: Ta_2O_5 88.38; Na_2O 11.62.

Analysis of potassium metatantalate.

Weights of substance 0.2026 and 0.2018 g.

Found %: Ta_2O_5 81.98, 82.32; K_2O 17.96, 17.64. $KTaO_3$. Calculated %: Ta_2O_5 82.43; K_2O 17.57.

Thermal Stability and Volatility of the Metatantalates of the Alkali Metals

Preliminary examination of the properties of the metatantalates showed that the latter had high melting points; it could therefore be surmised that their thermal stability was high.

The conditions under which the thermal stability was determined were similar to those employed for the thermal stability determinations of metaniobates.

TABLE 1

Effect of the Bond Character on the Melting Point of the Oxide and Its Volatility at 1200°

Oxide	Melting point	Loss in weight after 24 hours' ignition (in %)
MoO_3	795°	2.3
WO_3	1473	0.08
Nb_2O_5	1520	None
Ta_2O_5	1470	None

TABLE 2

Melting Point of Alkali Metal Salts of Molybdic, Tungstic, Niobic, and Tantallic Acids

Cation \ Anion	Melting point			
	NbO_3^{-1}	MoO_4^{-2}	TaO_3^{-1}	WO_4^{-2}
Li^{+1}	1164	705° [4]	>1200°	742° [3]
Na^{+1}	~1250	687	>1200	698
K^{+1}	1184	926	>1200	926
Rb^{+1}	~1200	929	>1200	959
Cs^{+1}	>1200	925	>1200	958

TABLE 3

Volatility of Niobates, Molybdates, Tantalates and Tungstates of the Alkali Metals at 1200° after 24 hours, expressed as %

Cation \ Anion	NbO_3^{-1}	MoO_4^{-2}	TaO_3^{-1}	WO_4^{-2}
Li^{+1}	None	0.73 [4]	None	0.43 [5]
Na^{+1}		1.84		0.25
K^{+1}		6.38		2.49
Rb^{+1}		11.92		5.72
Cs^{+1}		29.15		28.12

TABLE 4

Equivalent and Specific Electrical Conductivities of Aqueous Solutions of Metatantalates of the Alkali Metals at 25° (Cell constant 0.4439)

Compound	Electrical conductivity	
	Equivalent	Specific
$LiTaO_3$	$8.81 \cdot 10^{-5}$	$3.91 \cdot 10^{-5}$
$NaTaO_3$	$5.90 \cdot 10^{-5}$	$2.62 \cdot 10^{-5}$
$KTaO_3$	$7.61 \cdot 10^{-5}$	$3.28 \cdot 10^{-5}$
$RbTaO_3$	$7.55 \cdot 10^{-5}$	$3.25 \cdot 10^{-5}$
$CsTaO_3$	$6.08 \cdot 10^{-5}$	$2.70 \cdot 10^{-5}$

Results of ignition of all the anhydrous alkali metatantalates show that they do not possess appreciable volatility at a temperature of 1200°.

We also investigated the volatility of the same salts at the same temperature but in vacuum. The pressure in the apparatus was about 1 mm.

The duration of heating in this series of experiments was 2 and 6 hours. In all cases we found no change in weight of the metatantalates of the alkali metals.

The constancy of weight points to the thermal stability of all the salts and to the absence of volatility even in vacuum at 1200°. It should be mentioned that under these conditions the metatantalates do not melt and their color remains unchanged.

The thermal stability of metatantalates of the alkali elements may be explained by the bond strength of the TaO_3^{-1} ion. The oxygen ions, rigidly linked to the central tantalum atom, evidently do not exert a polarizing action on the alkali metal ions.

Our data for the thermal stability of anhydrous metaniobates and metatantalates of the alkali metals show that these compounds (with high melting temperatures of 1200° or higher) are lacking in volatility, evidently due to the ionic character of the bond [6].

It is interesting to compare the melting point and volatility of some compounds of molybdenum, tungsten, niobium and tantalum. Comparison of these values (Table 1), found for the oxides by Spitsyn and Shostak [3], shows that volatility is manifested by oxides of molybdenum and tungsten which have a less marked ionic character of bond than the oxides of niobium and tantalum.

The same picture is observed for salts of molybdic, tungstic, niobic and tantalic acids, as seen from the data set forth in Tables 2 and 3.

The lessening of the ionic character of the bond with gradual transition to a polar bond is usually associated with a decrease in the melting point of the salts and an increase in their volatility.

On the basis of the above facts, we may say that passage from niobates to molybdates and from tantalates to tungstates is accompanied by a change from an ionic to a polar character of bond.

Like the anhydrous alkali metal metaniobates, the corresponding metatantalates are sparingly soluble in water. We determined the equivalent and specific electrical conductivities of solutions of all the metantalates of the alkali metals saturated at 25°. Results of the measurements are set forth in Table 4. The results obtained bear a qualitative character.

The actual solubilities of these salts can only be obtained after determination of the mobility of the metatantalate ion or by the method of radioactive indicators.

SUMMARY

1. Anhydrous metatantalates of lithium, rubidium and cesium were prepared for the first time.
2. The thermal stability of all the anhydrous alkali metal metatantalates was studied; it was established that all these salts are thermally stable at 1200°.
3. The melting points of the metaniobates, molybdates, metatantalates and tungstates of the alkali metals were compared. Considerations about the causes of the stability of metaniobates and metatantalates of the alkali metals are put forward.

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Received February 2, 1954

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* T. p. = Consultants Bureau Translation Pagination.

PREPARATION OF THE SIMPLEST SODIUM CUPROTHIOSULFATES

G. A. Garkusha

The literature contains descriptions of salts with fairly diverse molar ratios of $\text{Cu}_2\text{S}_2\text{O}_3$, $\text{Na}_2\text{S}_2\text{O}_3$ and crystal water [4, 5, 7-10, 12, 13]. The following salts are also known:



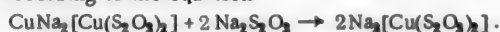
Rosenheim and Steinhauser [12] isolated the salts:



They also described more complex salts, for example:



to which Werner assigned the structure $(\text{NH}_4)_9[\text{Cu}(\text{S}_2\text{O}_3)_4\text{X}_2]$. Benrath [14] isolated a dark-blue salt $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{NH}_3$. Potassium salts known are $\text{K}_5[\text{Cu}(\text{S}_2\text{O}_3)_3 \cdot 3\text{H}_2\text{O}]$ and $\text{K}_7[\text{Cu}(\text{S}_2\text{O}_3)_4]$ which were isolated by Spacu and Murgulescu [15], and whose existence was denied by Ryabchikov on the grounds that a maximum of two thiosulfate residues can surround one atom of copper [1]. A paper by Ryabchikov and Silnichenko [2], indicated that the varying composition of the salt is due both to faulty conception of the mechanism of the reaction, in which, for the most part, no account was taken of the formation of an intermediate salt of $\text{Cu}_2\text{S}_2\text{O}_3$, and to the special characteristics of complex formation of copper compounds. According to the hypothesis advanced, only three types of complex salts must exist: $\text{Me}[\text{Cu}(\text{S}_2\text{O}_3)]$, $\text{Me}_4[\text{Cu}_2(\text{S}_2\text{O}_3)_3]$ and $\text{Me}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ with a coordination number of copper equal to 2. It was also observed that the properties of the salt NaCuS_2O_3 do not correspond to the properties described by other investigators. Thus, with ratios of copper sulfate to sodium thiosulfate of 1:2, a green solution is formed which contains the readily water-soluble salt NaCuS_2O_3 . To the yellow salt which is sparingly soluble in water is assigned the structure $\text{CuNa}_2[\text{Cu}(\text{S}_2\text{O}_3)_2]$ [2]. The latter was obtained by adding a saturated solution of copper sulfate to a saturated solution of sodium thiosulfate until the colorless solution turned green (i.e., as in the formation of the salt $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$). Finally, the preparation of this salt according to the equation



is unconvincing as a confirmation of the composition of the salt $\text{CuNa}_2[\text{Cu}(\text{S}_2\text{O}_3)_2]$, since this reaction also takes place with 2 moles of the salt NaCuS_2O_3 .

Since data for the composition and properties of the simplest sodium cuprothiosulfates are still conflicting, we decided to start this investigation. The literature describes the salt $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and water-insoluble, poorly stable salts with a yellow color: $\text{Cu}_2\text{S}_2\text{O}_3 \cdot \text{K}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\text{KCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}_2\text{S}_2\text{O}_3 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ or $\text{NH}_4\text{CuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Due to the varying valence of copper in the reaction of copper sulfate with sodium thiosulfate [11], when preparing the salt NaCuS_2O_3 it is necessary to take them in the ratio of 1:2.



Since the required salt is sparingly soluble in water, its yield must be close to the theoretical. On starting, however, from a 1:1 ratio, the yield of NaCuS_2O_3 must be nearly halved.

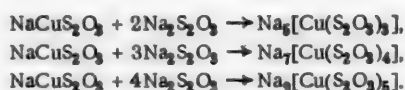
The salt $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ was prepared by us both directly, from copper sulfate, and from the salt $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In the former case the starting components will be taken in the ratio of 1:3.



In the second case the reaction proceeds according to the equation: $\text{NaCuS}_2\text{O}_3 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$.

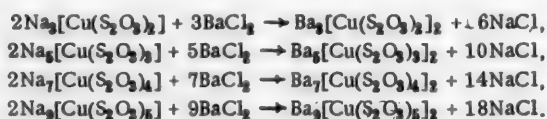
Since in the second case no by-products of the reaction are formed and the volume of reaction solution is very small, separation of the reaction product proceeds considerably more easily, the yields are better, and a purer salt is obtained. In both cases, however, precipitation with alcohol leads to formation of an oily reaction product. For this reason the isolation of the product is preferably effected by precipitation with alcohol in association with salting-out with sodium nitrate. The salt $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ is fairly stable in comparison with $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and the crystal water can be removed by drying at 90-95°. In aqueous solutions it decomposes after storing for many hours or (especially) on heating above 50°.

The salt $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ is adequately stable in a saturated aqueous solution of sodium thiosulfate both at room temperature and when heated to 60°. Both this observation and work on the salt of silver of analogous composition [3] served us as a basis for preparation of the salts $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$, $\text{Na}_7[\text{Cu}(\text{S}_2\text{O}_3)_4]$ and $\text{Na}_9[\text{Cu}(\text{S}_2\text{O}_3)_6]$. These were prepared according to the equations:



Aqueous solutions of these salts possess adequate stability in storage and when heated. Crystallization may occur in the solutions. The crystals are readily dehydrated, losing their water at 85-90°. By comparison with NaCuS_2O_3 and $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ they are much more stable. Thus, their aqueous solutions can be kept for several weeks without visible signs of decomposition, and they also resist heating to 80-90°. Of these three salts the least stable is $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$, and during its preparation it is therefore necessary to take a slight excess of sodium thiosulfate.

The composition of these three salts was verified by the preparation from them of the barium salts, and also the salt $\text{Ba}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]_2$:



These barium salts are sparingly soluble in water (about 1:3000), whereas the solubility of BaS_2O_3 is 1:480 (20°); therefore for titration with iodine a weighed sample of about 0.2 g is dissolved in 800 ml water with vigorous stirring for one to one and a half hours. The amount of potassium iodide taken is calculated on the basis of 4 g per 100 g solution; this avoids development of cloudiness toward the end of the addition of iodine and ensures stability of the blue color of the solution.

The barium salts resemble the sodium salts in respect of stability on keeping and heating.

EXPERIMENTAL •

Preparation of Sodium cuprothiosulfate $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

To 10 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 50 ml water was added a solution of 20 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 10 ml water until the blue color of the reaction solution changed to green, whereupon without delay about 1 ml 20% copper sulfate solution was run in to give a persistent green color. Formation of a yellow precipitate was accelerated by stirring. By the next day its amount had considerably increased and it was separated, washed 3 times with mother liquor diluted 1:1 with water (without allowing loss of crystals from the liquid), 3 times with the minimum amount of water, 5 times with 50% alcohol and 5 times with alcohol. Thorough washing improves the keeping quality of the crystals. Stability in storage depends upon the temperature. When the yellow crystals are kept in a refrigerator at 0-2°, their color does not change in the course of about 4 months. The weight of the air-dry precipitate was 7.7 g (89%). Drying of the crystals at 50-60° for only 30-40 minutes leads to their decomposition.

0.1910, 0.2560 g sub.: 8.8, 11.6 ml 0.1 N I_2 . 0.2020, 0.2076 g. sub.: 9.8, 10.0 ml 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.
Found %: S_2O_3 51.5, 50.6; Cu 30.8, 30.7. $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Calculated %: S_2O_3 51.8; Cu 29.4.

Preparation of sodium cuprodithiosulfate $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$.

5 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 20 ml water was added to a solution of 15 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 10 ml water. Into the filtered solution was introduced 7 g sodium nitrate, dissolved by stirring. 60 ml alcohol was added in portions and

• E. Ya. Karaulova participated in the analytical work.

on stirring a snow-white precipitate came down.

It was separated the next day, washed with alcohol and stirred with 70% alcohol, using not more than 60 ml of alcohol (excess of the latter results in a viscous mass). The precipitate was separated and washed, first with 70% alcohol until the test for nitrate was negative (test with diphenylamine), and again with alcohol. After drying in air with gradual rise of temperature from 50 to 90-95°, the weight of the precipitate was 5.3 g (66.5%).

0.1580, 0.1760 g sub.: 8.8, 9.9 ml 0.1 N I_2 . 0.2046, 0.2201 g sub.: 5.4, 6.0 ml 0.1 N $Na_2S_2O_3$. Found % S_2O_3 62.4, 62.8; Cu 16.8, 17.3. $Na_5[Cu(S_2O_3)_2]$. Calculated %: S_2O_3 63.0; Cu 17.85.

If the reaction product was separated with alcohol in the absence of sodium nitrate, an oily layer was formed which was collected and poured into a crystallizing dish after mixing with a fresh portion of alcohol. After 48 hours white crystals had formed and these were separated and mixed with alcohol (it was impossible to wash them with alcohol since a thick crust formed on the surface of the precipitate), again separated, and washed with alcohol.

Addition to 5 g $Na_2SO_3 \cdot 5H_2O$ in 5 ml water of 4.3 g $NaCuS_2O_3 \cdot H_2O$ with stirring gave a reaction solution from which, after working up in the above-described way, was separated a salt of the same composition $Na_5[Cu(S_2O_3)_2]$. To 1 g $Na_5[Cu(S_2O_3)_2]$, dissolved in 5 ml water, was added 30 ml 5% $BaCl_2$ solution. The resultant snow-white precipitate was separated, washed with water until the reaction for chlorine ion was negative and washed 5 times with alcohol. The snow-white crystals of $Ba_5[Cu(S_2O_3)_2]_2$ were dried to constant weight at 90-95°.

0.1840, 0.1920 g sub.: 0.1280, 0.1360 g $BaSO_4$. 0.2180, 0.2220 g sub.: 4.0, 4.2 ml 0.1 N $Na_2S_2O_3$. 0.1840, 0.2040 g sub.: 7.3, 8.2 ml 0.1 N I_2 . Found %: Ba 40.8, 41.7; Cu 12.4, 12.0; S_2O_3 44.4, 44.9. $Ba_5[Cu(S_2O_3)_2]_2$. Calculated %: Ba 41.7; Cu 12.88; S_2O_3 45.5.

Preparation of sodium tricaprothiosulfate $Na_5[Cu(S_2O_3)_3]$

To a solution of 25 g $Na_2S_2O_3 \cdot 5H_2O$ in 15 ml water was added portionwise with stirring 10.8 g $NaCuS_2O_3 \cdot H_2O$ until completely dissolved. The solution was evaporated at 40° and then in succession at 50, 60 and 80° until a precipitate had been obtained either in the form of a thick slurry or of a solid. The precipitate was dissolved in the minimum amount of water and filtered, and the water removed in the manner described above. After drying to constant weight at 90-95° the precipitate weighed 23.5 g (90%).

0.2355, 0.2353 g sub.: 4.4, 4.3 ml 0.1 N $Na_2S_2O_3$. 0.1940, 0.1787 g sub.: 11.2, 10.4 ml 0.1 N I_2 . Found %: S_2O_3 64.6, 65.1; Cu 11.8, 11.65. $Na_5[Cu(S_2O_3)_3]$. Calculated %: S_2O_3 65.4; Cu 12.35.

The barium salt was prepared from a 10% solution of $Na_5[Cu(S_2O_3)_3]$ and a 5% solution of $BaCl_2$ taken in the stoichiometric ratio.

0.2146, 0.2090 g sub.: 0.1650, 0.1630 g $BaSO_4$. 0.1620, 0.1650 g sub.: 2.2, 2.3 ml 0.1 N $Na_2S_2O_3$. 0.2006, 0.3043 g sub.: 8.0, 12.0 ml 0.1 N I_2 . Found %: Ba 45.3, 45.9; Cu 8.9, 8.8; S_2O_3 44.7, 44.0. $Ba_5[Cu(S_2O_3)_3]_2$. Calculated %: Ba 46.2; Cu 8.55; S_2O_3 45.3.

Preparation of sodium tetracaprothiosulfate $Na_7[Cu(S_2O_3)_4]$

To a solution of 11.25 g $Na_2S_2O_3 \cdot 5H_2O$ in 6 ml water was added 3.24 g $NaCuS_2O_3 \cdot H_2O$. The conditions for carrying out the reaction and for isolation of the product were the same as for $Na_5[Cu(S_2O_3)_3]$. Weight of salt 8 g (80%).

0.3214, 0.2434 g sub.: 18.9, 14.5 ml 0.1 N I_2 . 0.2622, 0.1982 g sub.: 4.1, 3.1 ml 0.1 N $Na_2S_2O_3$. Found %: S_2O_3 65.8, 63.7; Cu 9.92, 9.93. $Na_7[Cu(S_2O_3)_4]$. Calculated %: S_2O_3 66.8; Cu 9.45.

The barium salt was prepared in the same way as for $Ba_5[Cu(S_2O_3)_3]_2$.

0.2880, 0.2680 g sub.: 0.2323, 0.2160 g $BaSO_4$. 0.1888, 0.2680 g sub.: 1.9, 2.6 ml 0.1 N $Na_2S_2O_3$. 0.1988, 0.2080 g sub.: 7.9, 8.0 ml 0.1 N I_2 . Found %: Ba 47.4, 47.5; Cu 6.4, 6.1; S_2O_3 44.5, 44.1. $Ba_7[Cu(S_2O_3)_4]_2$. Calculated %: Ba 48.33; Cu 6.4; S_2O_3 45.1.

Preparation of sodium pentacaprothiosulfate $Na_9[Cu(S_2O_3)_5]$

To a solution of 15 g $Na_2S_2O_3 \cdot 5H_2O$ in 7 ml water was added 3.24 g $NaCuS_2O_3 \cdot H_2O$. The conditions for carrying out the reaction and for separating the product were the same as for $Na_5[Cu(S_2O_3)_3]$. After drying to constant weight the crystals weighed 11.6 g (94.5%).

0.3095, 0.3200 g sub.: 18.3, 19.0 ml 0.1 N I_2 . 0.2440, 0.2660 g sub.: 2.7, 2.8 ml 0.1 N $Na_2S_2O_3$. Found %: S_2O_3 66.2, 66.4; Cu 7.0, 6.7. $Na_9[Cu(S_2O_3)_5]$. Calculated %: S_2O_3 67.4; Cu 7.65.

The barium salt was prepared as described for $Ba_5[Cu(S_2O_3)_3]_2$.

0.3020, 0.2820 g sub.: 0.2520, 0.2340 g $BaSO_4$. 0.1930, 0.2306 g sub.: 1.4, 1.8 ml 0.1 N $Na_2S_2O_3$. 0.2010, 0.2002 g sub.: 8.0, 7.9 ml 0.1 N I_2 . Found %: Ba 49.2, 48.8; Cu 4.6, 4.97; S_2O_3 44.5, 44.1. $Ba_9[Cu(S_2O_3)_5]_2$. Calculated %: Ba 49.72; Cu 5.12; S_2O_3 45.08.

SUMMARY

1. The methods for preparation of $\text{NaCuS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Na}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$ have been improved.
2. Methods are presented for preparation of the previously undescribed salts: $\text{Na}_6[\text{Cu}(\text{S}_2\text{O}_3)_3]$, $\text{Na}_7[\text{Cu}(\text{S}_2\text{O}_3)_4]$, $\text{Na}_9[\text{Cu}(\text{S}_2\text{O}_3)_5]$, $\text{Ba}_3[\text{Cu}(\text{S}_2\text{O}_3)_2]$, $\text{Ba}_5[\text{Cu}(\text{S}_2\text{O}_3)_3]$, $\text{Ba}_7[\text{Cu}(\text{S}_2\text{O}_3)_4]$ and $\text{Ba}_9[\text{Cu}(\text{S}_2\text{O}_3)_5]$.

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Received February 9, 1954.

REACTIONS IN SOLUTIONS BETWEEN ZIRCONIUM NITRATE AND ALKALI METAL IODATES. I.

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Composition of freshly precipitated zirconium iodate. The first publication on the composition of zirconium iodate was that of Davis [1] who prepared zirconium oxyiodates of indeterminate composition. Venable and Smithey [2] also separated precipitates of indeterminate composition [between $Zr_2O_4(IO_3)_4$ and $Zr_4O_7(IO_3)_2$]. They suggested that they did not isolate the normal zirconium iodate [$ZrO(IO_3)_2$] because this salt is strongly hydrolyzed when washed with water.

In 1941 Chemikov and Uspenskaya [3] reported that precipitation of zirconium from nitrate solutions gives iodates of variable composition. According to their data, one can also obtain precipitates of definite composition, for example



by strictly adhering to the conditions established by them. On this basis the authors recommended a volumetric iodometric method of determination of zirconium.

Handbooks [4] report that on standing of zirconium iodate precipitates with the mother liquors for a long time, compounds are formed which contain 7.5 to 9 iodate groups per atom of zirconium. No indication is given of the character and properties of such compounds.

It appears from the literature data that the study of the composition of zirconium iodate precipitates has been inadequate. No systematic investigations have been undertaken, so that it is difficult to judge the correctness of existing data for the composition of zirconium iodate.

EXPERIMENTAL

Experimental method*. Use was made in the experiments of standard aqueous or nitric acid solutions of zirconium nitrate and potassium iodate. The precipitates of zirconium iodate were prepared by adding potassium iodate solution to zirconium nitrate solution. In some experiments dry potassium iodate was also added.

The number of iodate groups combining with zirconium was determined by analyzing the precipitates and by back-titration.

To an accurately measured volume of standard zirconium nitrate solution was added an accurately measured volume of standard (in respect of IO_3^-) potassium iodate solution. The resultant precipitate (fresh or after standing) was separated from the mother liquor. The mother liquor was collected separately from the wash waters. An aliquot portion of the mother liquor was taken for determination of iodate ions which had not reacted with zirconium. The iodometric method was employed.

From the difference between the amount of potassium iodate (iodate ions) taken and the amount remaining in solution, the amount of iodate which had reacted with zirconium was determined. The fall in the iodate ion content of the solution was related to the amount of zirconium isolated in the precipitate. Similar calculations can also be based on data for the fall in concentration of iodate ions and of zirconium in solution due to formation of zirconium iodate.

The precipitate was washed with water, or with alcohol and ether, or with acid, alcohol and ether, and it was then dried at room temperature. Zirconium and iodate groups were determined in weighed amounts of the air-dry precipitate. The analytical results gave the ratio between zirconium and iodate groups.

Comparison of the ratios between zirconium and iodate groups found by analysis of the precipitate with those determined by back-titration permitted evaluation of the suitability of the wash liquids tested.

* The procedures described refer both to freshly brought-down precipitates and to those which have stood in contact with the mother liquors.

Back-titration was used by choice in experiments carried out with a large excess of added potassium iodate, when the zirconium came down quantitatively. When the zirconium did not come down completely, the results were corrected from determinations of the zirconium in the mother liquors.

On the basis of back titration, 3 N HNO_3 was selected as the wash liquid. Water and alcohol were found unsuitable.

After the precipitate had been separated by centrifuging, it was washed 5-6 times with wash liquid, 2-3 times with alcohol (95% by volume) and 2-3 times with ether. Washing with nitric acid completely eliminated the excess potassium iodate; the alcohol got rid of the nitric acid, and the ether removed the alcohol.

As was pointed out, the precipitates were analyzed for potassium, zirconium and iodate groups. In some precipitates the content of crystal water was also determined by drying at 90-95°, and also the nitrate content by Devarda's method under the conditions described by Hillebrand and Lendel [5]. For the latter analysis, instead of 2.5 g Devarda alloy, 4 g was taken to allow for its consumption for reduction of iodate to iodide.

Zirconium was determined in 400-500 mg precipitate; this was dissolved in 5 ml concentrated hydrochloric acid, diluted to about 100 ml with distilled water, and then the iodate was reduced to iodide with 30% hydroxylamine solution. After decomposition of the iodate, the zirconium was precipitated with ammonia and the precipitated hydrous oxide was, as usual, washed, ignited, and dried.

The potassium was determined in the filtrate from the zirconium hydroxide. The filtrate was first evaporated to a small volume in a beaker, and the residue of liquid was transferred to a weighed porcelain crucible and evaporated to dryness. The dry residue was dissolved in a small volume of distilled water, whereupon addition was made to the solution of 2-3 drops of 30% hydroxylamine solution. In the event of iodate being found in the dry residue (separation of free iodine), the treatment with hydroxylamine was repeated until the iodate had been entirely converted into hydriodic acid and it had been removed by evaporation from the hydrochloric acid solution.

The residual potassium chloride was ignited to constant weight, and the amount of potassium in the weighed sample of zirconium iodate precipitate taken was calculated. The potassium content was also determined by the chloroplatinate method.

The number of iodate groups entering into the composition of the precipitate was determined iodometrically on a 60-80 mg sample. The weighed sample of iodate precipitate in a weighing bottle was dissolved in 2.5 ml concentrated (or 5 ml 1:1 diluted) sulfuric acid (complete solution of the precipitate sometimes called for brief heating on a water bath). The sulfuric acid solution was diluted with water to 250 ml, 1 g dry potassium iodide was added, and the liberated iodine was titrated with an 0.05N (or slightly stronger) sodium thiosulfate solution in presence of starch. The titer of the thiosulfate was determined under the same conditions.

Numerical results of analysis of the zirconium iodate precipitates were obtained in not fewer than two experiments (in each case) carried out under identical conditions.

Compositions of precipitates of freshly precipitated zirconium iodates. The starting solution of zirconium nitrate contained 1.4 g zirconium per liter. All the experiments were carried out at room temperature, which varied between +15 and +25°. Results are set forth in the table. When examining the tabulated data it must be remembered that at low concentrations of potassium iodate in the nitric acid solutions, the zirconium partly came down in the precipitate. The zirconium iodate has a variable composition, which changes with changing concentration of potassium iodate and with changing acidity. At low acidities of the solutions (pH 2-3) the potassium iodate concentration of the solution scarcely influenced the composition of the precipitate. Moniodate comes down both with large and small additions of potassium iodate (experiments 1-4). Only with very large excesses of potassium iodate in the solution was up to 1.3 iodate groups per atom of zirconium found in the precipitate (experiment 4), and this was evidently due to adsorption of potassium iodate by the voluminous precipitate of zirconium moniodate.

If the acidity of the solution is not too low, the composition of the precipitates depends in the main on the excess of added potassium iodate. With low concentrations of potassium iodate, part of the zirconium present in the solution forms moniodate and is thereby brought down, while the other part remains in solution (experiments 5, 11, 15 and 21). The lower the acidity of the solution, the greater is the proportion of zirconium which may be brought down as moniodate. The conditions under which zirconium is quantitatively brought down in the precipitate in the form of moniodate have been noted above.

On addition of a large excess of potassium iodate to nitric acid solutions of zirconium, only zirconium triiodate is detected in the precipitates. Formation of triiodate is observed over a wide range of acidities and excesses of added potassium iodate (experiments 10, 14, 18-20, 24 and 25).

By regulation of the excess of added potassium iodate it is possible to obtain from the nitric acid solutions precipitates of intermediate compositions with a content of more than one and less than three iodate groups per atom of

Composition of freshly precipitated zirconium iodates

Zirconium concentration in the final volume 0.00762 mole/liter (0.695 g/liter)

Experiment No.	Concentration of IO_3^- (in g-ions/liter)		Fall in concentration of IO_3^- in solution (by difference)	Content in precipitate (in %)				Ratio of $\text{Zr} : \text{IO}_3 : \text{H}_2\text{O}$
	Before precipitation of the zirconium	After precipitation of the zirconium		Zr	IO_3^-	Total	H_2O (by difference)	
pH 2.25								
1	0.0097	0.0042	0.0055	22.93	46.07	69.00	31.00	1 : 1.05 : 6.83
2	0.064	0.0562	0.0078	22.32	47.10	69.42	30.58	1 : 1.10 : 6.94
3	0.107	0.097	0.010	20.91	48.93	69.84	30.16	1 : 1.28 : 7.31
4	0.161	0.152	0.009	20.68	50.89	71.57	28.43	1 : 1.28 : 6.97
0.07 N HNO_3								
5	0.008	0.0079	0.0001	23.27	41.68	65.95	35.05	1 : 0.93 : 7.63
6	0.024	0.010	0.014	16.60	63.99	80.59	19.41	1 : 2.01 : 5.92
7	0.050	0.032	0.018	14.61	68.23	82.84	17.16	1 : 2.43 : 5.95
8	0.077	0.056	0.021	13.71	69.24	82.95	17.05	1 : 2.63 : 6.30
9	0.111	0.089	0.022	13.65	74.12	87.77	12.23	1 : 2.83 : 4.54
10	0.152	0.129	0.023	13.51	76.06	89.57	10.43	1 : 2.94 : 3.91
0.5 N HNO_3								
11	0.0113	0.0070	0.0043	21.89	48.40	70.29	29.71	1 : 1.15 : 6.88
12	0.0206	0.0054	0.015	16.71	64.36	81.07	18.93	1 : 2.03 : 5.74
13	0.033	0.015	0.018	14.62	67.24	81.86	18.14	1 : 2.40 : 6.29
14	0.061	0.040	0.021	12.85	73.25	86.10	13.90	1 : 2.94 : 5.48
0.99 N HNO_3								
15	0.015	0.015	—	23.02	45.58	68.60	31.40	1 : 1.03 : 6.91
16	0.026	0.008	0.018	17.78	60.45	78.29	21.77	1 : 1.77 : 6.20
17	0.045	0.023	0.022	13.41	72.81	86.22	13.78	1 : 2.83 : 5.21
18	0.054	0.031	0.023	12.89	74.12	87.01	12.99	1 : 3.00 : 5.11
19	0.077	0.053	0.024	12.81	75.58	88.39	11.61	1 : 3.08 : 4.57
20	0.350	0.327	0.023	12.77	76.62	89.33	10.67	1 : 3.13 : 4.23
5 N HNO_3								
21	0.037	0.037	—	23.09	44.11	67.20	32.80	1 : 0.96 : 7.20
22	0.051	0.035	0.016	15.02	67.14	82.16	17.84	1 : 2.33 : 5.73
23	0.059	0.014	0.019	13.30	74.08	87.38	12.62	1 : 2.90 : 4.81
24	0.086	0.063	0.023	12.90	76.06	88.96	11.04	1 : 3.07 : 4.34
25	0.571	0.547	0.024	12.70	76.29	88.99	11.01	1 : 3.13 : 4.39

zirconium. The majority of these precipitates are evidently mixtures into which, in particular, enter zirconium monoiodate and triiodate. When a very high concentration of potassium iodate is formed in the solution, a portion of the zirconium (still in solution) forms triiodate, and at the same time other precipitates which react with the potassium iodate present in solution are also transformed into triiodate. Consequently, when zirconium is precipitated from very weakly acidic solutions, the stable precipitates are monoiodates, while on precipitation from solutions containing a considerable amount of acid the stable precipitates are triiodates.

Stable precipitates of zirconium tetraiodate are not formed, at least not at acidities up to 7.5 N and with any given concentration of potassium iodate in solution. Potassium and nitrate groups do not enter into the composition of iodates which have been freshly precipitated and left for short periods (1-1½ hours). Consequently the freshly precipitated zirconium iodates are hydroxy compounds. The monoiodate and triiodate can be dried to constant weight at 90-95°; during the operation the precipitates turn slightly brown, indicating partial breakdown at these temperatures. The loss of weight of the monoiodate during drying corresponds to the removal of 4.25 to 4.40 molecules water; that of the triiodate to 3.90-4.10 molecules.

Taking into consideration the difficulties resulting from partial decomposition of zirconium iodates during drying, we may assume that the monoiodate and triiodate each contain 4 molecules of crystal water. Experiments 1-4, 11, 15 and 21 show that in air-dry samples of zirconium monoiodate the total content of zirconium and iodate groups is 69-70%; the remaining 31-30% corresponds to a content of roughly 7 molecules of water (or 3 hydroxyl groups, which are not lost on drying, and 4 molecules of water which are lost at 90-95°). In the triiodate the over-all content of zirconium and iodate groups is 88%.

On the basis of the analytical data, the composition of zirconium monoiodate may be represented by $Zr(OH)_2IO_3 \cdot 4H_2O$, and that of the triiodate by $ZrOH(IO_3)_3 \cdot 4H_2O$.

Zirconium diiodate was not isolated, although it is reasonable to assume that it exists and comes down from nitric acid solutions after precipitation of the monoiodate. Zirconium diiodate must have the following composition: $Zr(OH)_2(IO_3)_2 \cdot 4H_2O$. When a large excess of potassium iodate is added, the diiodate (like the monoiodate) changes into triiodate.

SUMMARY

1. Addition of potassium iodate to a solution of zirconium nitrate causes precipitation of a hydroxy compound containing from one to three iodate groups per atom of zirconium. The amount of combining iodate ions depends upon the amount of added potassium iodate as well as on the acidity of the solution. When potassium iodate is used as the precipitant, zirconium does not form stable precipitates of tetraiodate.

2. When zirconium is precipitated from an aqueous solution of its nitrate with an aqueous solution of potassium iodate (pH of the mixture of solutions 2-3) the monoiodate $Zr(OH)_2IO_3 \cdot 4H_2O$ is formed. The composition of the precipitates changes somewhat with a large excess of potassium iodate in the solution, probably due to adsorption of potassium iodate.

3. Zirconium comes down from nitric acid solutions in the form of an iodate of variable composition. When a small amount of potassium iodate is added, part of the zirconium comes down as the monoiodate with composition as above. When a large excess of potassium iodate is added, only the triiodate $ZrOH(IO_3)_3 \cdot 4H_2O$ is detected in the precipitate.

By regulating the excess of added potassium iodate, it is possible to obtain precipitates with intermediate compositions containing more than one and less than three iodate groups per atom of zirconium.

4. Zirconium triiodate is formed from zirconium nitrate as well as from precipitates of hydroxyiodates containing fewer than three iodate groups per atom of zirconium. In the latter case, the hydroxyl groups (all but one) are replaced by iodate groups. Zirconium triiodate is formed over wide intervals of acidities and of concentrations of potassium iodate in the solution.

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Received December 27, 1953

REACTION OF BARIUM TITANATE WITH FLUORIDES AND PYROPHOSPHATES OF SODIUM AND POTASSIUM

M.L. Sholokhovitch and I.N. Belyaev

Sodium fluorides and pyrophosphates are some of the best solvents for barium titanate in melts [1]. For this reason the investigation of the reaction of BaTiO_3 with these salts in melts is a matter of special interest both for the purposes of growing single crystals of BaTiO_3 from molten media and for clarification of the mechanism of reaction of fluorides and pyrophosphates with barium titanate, the chemistry of which has hitherto received little consideration. The need for a many-sided approach to the investigation of the properties of BaTiO_3 has already been demonstrated [2, 3].

Melts of BaTiO_3 with fluorides and pyrophosphate of sodium or potassium are complex multicomponent systems (Na , Ba , TiO_3 , F , P_2O_7). Graphically such systems may be represented by prisms (Fig. 1). In this paper we submit the results of investigation by the visual-polythermic method of fusion to 1100° of the internal sections of these prisms; namely, the sections $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ and $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$.

Starting substances. Polycrystalline BaTiO_3 was prepared by two fusions of chemically pure BaCO_3 with TiO_2 in stoichiometric ratios; the sodium and potassium fluorides were analytically pure grades with melting points of 982° (NaF) and 865° (KF). Sodium and potassium pyrophosphates were prepared by igniting chemically pure Na_2HPO_4 and K_2HPO_4 . The melting points were 994° ($\text{Na}_4\text{P}_2\text{O}_7$) and 1099° ($\text{K}_4\text{P}_2\text{O}_7$). All data are expressed in equimolar percentages.

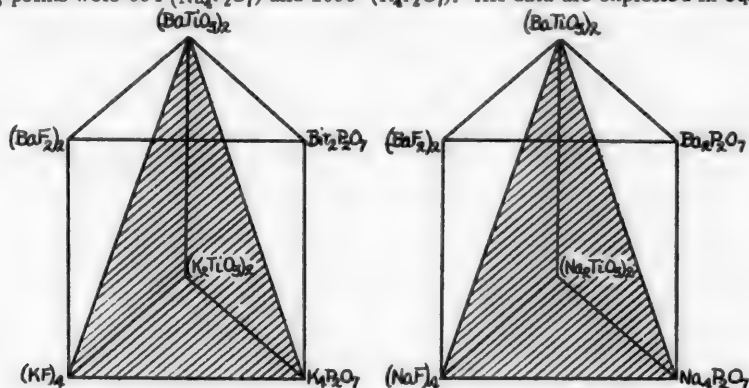


Fig. 1. Prisms of the complex systems Na , $\text{Ba} \parallel \text{TiO}_3$, F , P_2O_7 and K , $\text{Ba} \parallel \text{TiO}_3$, F , P_2O_7 .

Section of $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$

The sides $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_4\text{F}_4 - (\text{BaTiO}_3)_2$ (Figs. 2 and 3) are simple eutectic systems.

The side $\text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ (Fig. 2) is not a stable section of the reciprocal system $(\text{BaTiO}_3)_2 + \text{Na}_4\text{P}_2\text{O}_7 = \text{Ba}_2\text{P}_2\text{O}_7 + (\text{Na}_2\text{TiO}_3)_2$.

Optical examination of the phases crystallizing in the system in the range up to 1100° failed to reveal crystals of BaTiO_3 . 10 internal cuts through the system $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ were investigated. Data for the cuts are set forth in Table 1.

The surface of crystallization of the section $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ up to 1100° is represented in Fig. 4. Fig. 5 is the projection of the lines of common crystallization of the system on the side $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7$.

It follows from the data obtained that the surface of crystallization of the section $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ up to a temperature of 1100° comprises four fields:

- 1) $\text{Na}_4\text{P}_2\text{O}_7$ and 2) NaF , occupying respectively 3.05 and 8.10% of the area of the system; 3) phases not established

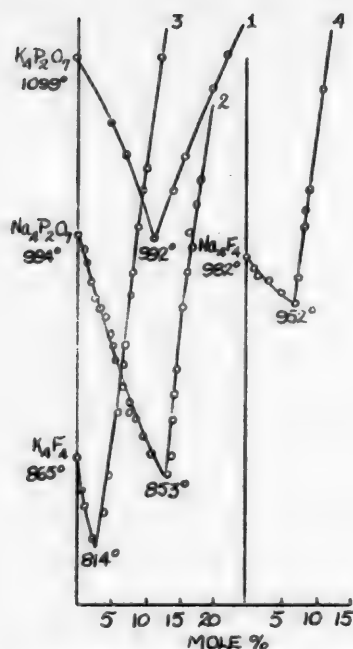


Fig. 2. Sides of sections through the complex systems. 1) $K_4P_2O_7 - (BaTiO_3)_2$, 2) $Na_4P_2O_7 - (BaTiO_3)_2$, 3) $K_4F_4 - (BaTiO_3)_2$, 4) $Na_4F_4 - (BaTiO_3)_2$.

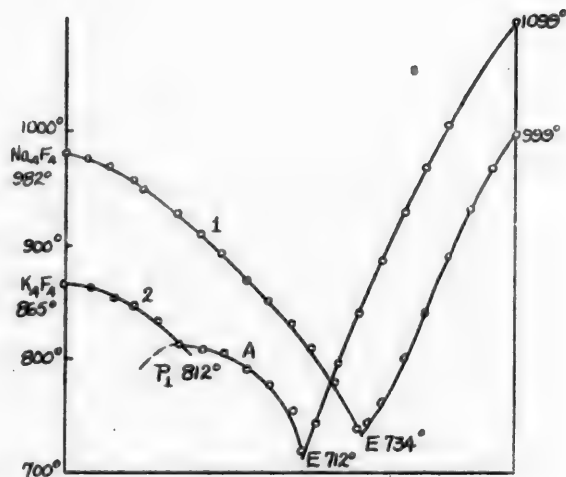


Fig. 3. Sides of sections through the complex systems. 1) $Na_4F_4 - Na_4P_2O_7$, 2) $K_4F_4 - K_4P_2O_7$. E) eutectic points; P_1 —transition point; A— $3K_4F_4 \cdot K_4P_2O_7$.

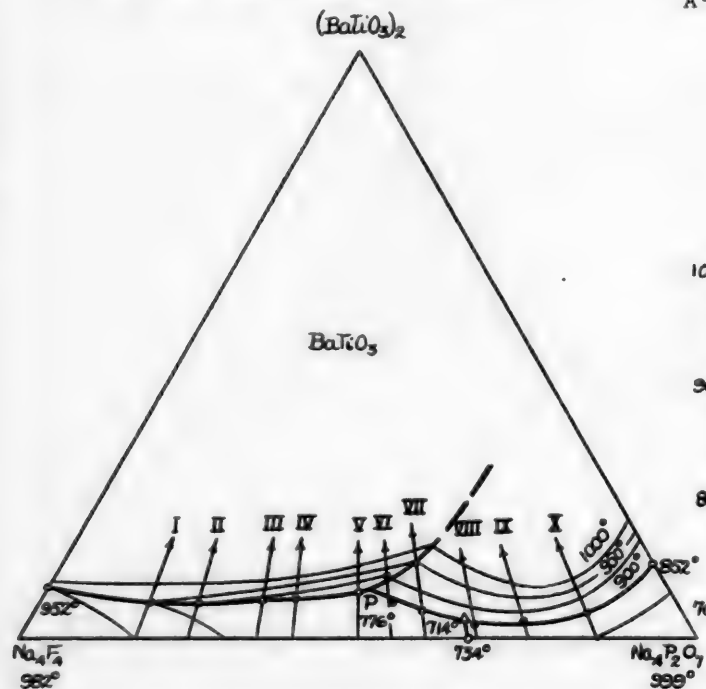


Fig. 4. Surface of crystallization of the section $Na_4F_4 - Na_4P_2O_7 - (BaTiO_3)_2$. Explanation in text.

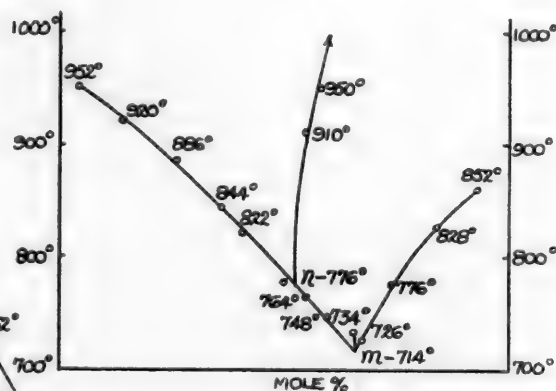


Fig. 5. Projection of lines of common crystallization on the side of sodium fluoride and pyrophosphate. Explanation in text.

by us; and 4) $BaTiO_3$, occupying the greater part of the system. The system contains two quaternary, univariant points: point n corresponding to 48% $Na_4P_2O_7$, 8% $BaTiO_3$, 44% NaF and 776°, and point m, corresponding to 64% $Na_4P_2O_7$, 3.5% $BaTiO_3$, 32.5% NaF and 714°.

TABLE 1

Special points of the internal cuts

Cut Number	Composition of starting mixture of cuts in the direction of barium titanate	Points of intersection of branches of crystallization of the various phases		
		Point No.	BaTiO (mole-%)	Temperature
To section $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - \text{Ba}(\text{TiO}_3)_2$				
I	82.5% Na_4F_4 + 17.5% $\text{Na}_4\text{P}_2\text{O}_7$		5.5	920°
II	75% Na_4F_4 + 25% $\text{Na}_4\text{P}_2\text{O}_7$		5.0	886
III	65% Na_4F_4 + 35% $\text{Na}_4\text{P}_2\text{O}_7$		6.5	844
IV	60% Na_4F_4 + 40% NaP_2O_7		6.5	822
V	50% Na_4F_4 + 50% $\text{Na}_4\text{P}_2\text{O}_7$		8.0	776
VI	45% Na_4F_4 + 55% $\text{Na}_4\text{P}_2\text{O}_7$	1	4.5	764
		2	10.0	910
VII	40% Na_4F_4 + 60% $\text{Na}_4\text{P}_2\text{O}_7$	1	3.5	748
		2	12.5	950
VIII	32.5% Na_4F_4 + 67.5% $\text{Na}_4\text{P}_2\text{O}_7$		1.5	726
IX	25% Na_4F_4 + 75% $\text{Na}_4\text{P}_2\text{O}_7$		2.5	776
X	15% Na_4F_4 + 85 % $\text{Na}_4\text{P}_2\text{O}_7$		3.5	828
To section $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$				
I	90% K_4F_4 + 10% $\text{K}_4\text{P}_2\text{O}_7$		4.5	798
II	80% K_4F_4 + 20% $\text{K}_4\text{P}_2\text{O}_7$		8.5	770
III	77.5% K_4F_4 + 22.5% $\text{K}_4\text{P}_2\text{O}_7$	1	5.5	776
		2	9.0	768
IV	74% K_4F_4 + 26% $\text{K}_4\text{P}_2\text{O}_7$	1	2.5	776
		2	9.0	790
V	70% K_4F_4 + 30% $\text{K}_4\text{P}_2\text{O}_7$	1	3.0	770
		2	9.5	832
VI	60% K_4F_4 + 40% $\text{K}_4\text{P}_2\text{O}_7$	1	2.5	753
		2	12.5	796
VII	50% K_4F_4 + 50% $\text{K}_4\text{P}_2\text{O}_7$		1.5	710
VIII	40% K_4F_4 + 60% $\text{K}_4\text{P}_2\text{O}_7$		1.5	745
IX	30% K_4F_4 + 70% $\text{K}_4\text{P}_2\text{O}_7$		2.0	804
X	25% K_4F_4 + 75% $\text{K}_4\text{P}_2\text{O}_7$		2.5	920
XI	15% K_4F_4 + 85% $\text{K}_4\text{P}_2\text{O}_7$		4.5	980

Field Number	Name	Area occupied by each field as percentage of the total surface of the system	Due to the high crystallization temperatures, the boundaries of the fields could not be completely delineated	Due to the high crystallization temperatures, the boundaries of the fields could not be completely delineated
1	KF	2.13		
2	$3\text{K}_4\text{F}_4 \cdot \text{K}_4\text{P}_2\text{O}_7$	1.74		
3	$\text{K}_4\text{P}_2\text{O}_7$	4.37		
4	Phase not accurately determined			
5	BaTiO_3			

TABLE 2

Field Number	Name	Area occupied by each field as percentage of the total surface of the system
1	KF $3\text{K}_4\text{F}_4 \cdot \text{K}_4\text{P}_2\text{O}_7$ $\text{K}_4\text{P}_2\text{O}_7$ Phase not accurately determined	2.13
2		1.74
3		4.37
4		
5	BaTiO_3	

Consequently, the system $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ is an unstable section of the prism. For the purpose of growth of single crystals of BaTiO_3 from compositions heated to a maximum of 1100°, use may be made of the compositions $[\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7] - (\text{BaTiO}_3)_2$, in which the amount of $\text{Na}_4\text{P}_2\text{O}_7$ does not exceed 50%.

Section $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$

Of the sides of the section, only the side of $\text{K}_4\text{F}_4 - (\text{BaTiO}_3)_2$ (Fig. 2) is a simple eutectic system. The side $\text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ (Fig. 2) evidently contains a product of exchange; it was optically established that the phase crystallizing at temperatures between 814 and 1100° is not barium titanate. In the system $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7$ (Fig. 3) there is formed, in contrast to the corresponding sodium system, a compound $3\text{K}_4\text{F}_4 \cdot \text{K}_4\text{P}_2\text{O}_7$, melting with decomposition at 812°. An investigation was made of 11 internal cuts (see table). In Fig. 6 is represented the surface of crystallization up to 1100° of the system $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$. In Fig. 7 is shown the projection of the surface of crystallization of this system on to the $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7$ side. We see that the surface of crystallization of the section $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ comprises five fields (Table 2).

The greater part of the surface of the system is occupied by BaTiO_3 .

In the section $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ field 4 (evidently an exchange product) has penetrated deeply into the system. The system contains 3 univariant points; point m_1 at 19% $\text{K}_4\text{P}_2\text{O}_7$, 70.5% KF , 10.5% BaTiO_3 and 780°, n at 24% $\text{K}_4\text{P}_2\text{O}_7$, 73.5% KF , 2.5% BaTiO_3 , 768°; and point m_2 at 54% $\text{K}_4\text{P}_2\text{O}_7$, 45% KF , 1.0% BaTiO_3 and 695°.

It should be noted that on cooling of compositions corresponding to cut II $80\% \text{K}_4\text{F}_4 + 20\% \text{K}_3\text{P}_2\text{O}_7 \rightarrow (\text{BaTiO}_3)_2$, the barium titanate crystallizes considerably more easily than on cooling of melts consisting only of a mixture of KF and $(\text{BaTiO}_3)_2$. On complete cooling of mixtures corresponding in composition to cut II, two layers are clearly formed, the upper one of which is BaTiO_3 .

SUMMARY

1. A study was made up to 1100° by the visual-polythermic method of the surface of crystallization of the systems $\text{Na}_4\text{F} - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ and $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$.

2. In the binary system $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7$, in contrast to the corresponding system with participation of sodium salts, was found a compound $3\text{K}_4\text{F}_4 \cdot \text{K}_4\text{P}_2\text{O}_7$ which melts with decomposition and also appears conspicuously inside the section $\text{K}_4\text{F}_4 - (\text{BaTiO}_3)_2 - \text{K}_4\text{P}_2\text{O}_7$.

3. It was established that the systems $\text{Na}_4\text{F}_4 - \text{Na}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ and $\text{K}_4\text{F}_4 - \text{K}_4\text{P}_2\text{O}_7 - (\text{BaTiO}_3)_2$ are unstable sections of the prisms $\text{Na, Ba} \parallel \text{F, P}_2\text{O}_7, \text{TiO}_3$ and $\text{K, Ba} \parallel \text{F, P}_2\text{O}_7, \text{TiO}_3$.

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Received March 25, 1954

Rostov-on-Don State University

* T.p. = C B. Translation pagination.

THE PREPARATION AND SOME PROPERTIES OF PHOSPHO-9-
MOLYBDATES (LUTEOPHOSPHOMOLYBDATES) OF RUBIDIUM AND CESIUM

E.A. Nikitina and O.N. Sokolova

Some heteropoly acids give difficultly soluble rubidium and cesium salts and fairly highly soluble salts of potassium, sodium and magnesium. Investigation of the composition and solubility of these rubidium and cesium salts is of definite interest.

In the foreign literature [1] a method was published some while ago for quantitative determination of rubidium and cesium with the help of luteophosphomolybdic acid. Since we have worked out in detail [2] a method of preparation of this heteropoly acid, and since its potassium and sodium salts are soluble, it appeared expedient to make a critical evaluation of the proposed method.

The authors of the paper, O'Leary and Papish, described a method of preparation of luteophosphomolybdic acid $H_{12}[P_2O_5(Mo_2O_7)_9] \cdot xH_2O$, which consisted in heating commercial phosphomolybdic acid $H_7[P(Mo_2O_7)_6] \cdot xH_2O$ at 300-350° with continuous stirring until the yellow color had changed completely to green; the cooled acid was extracted with water; the reduced solution was oxidized with bromine water and slowly evaporated. Large yellow crystals came down which the authors assumed to be luteophosphomolybdic acid. They did not report an analysis of the crystals.

Precipitation of rubidium and cesium was effected with the help of luteophosphomolybdic acid prepared in the above fashion.

An attempt by the authors to establish the formula of the prepared cesium salt revealed that it is closer to the composition of the hexa-substituted salt than to the dodeca-substituted salt. As the authors admit, the analysis cannot be considered satisfactory since the composition of preparations obtained in presence of excess of one of the components differs from that of preparations isolated in presence of an excess of the other. Moreover, in both cases the sum of the components was less than 100% if reckoned on the MoO_3 and more if reckoned on the Mo_2O_7 .

The cesium content of the prepared samples was 15 and 17%, calculated on the anhydrous composition. Instead of representing the composition of the salt by the appropriate formula on the basis of analysis of the prepared salt, the authors (ignoring the analytical data) assumed that they had obtained an actual salt of luteophosphomolybdic acid, and they attributed to it the formula $Cs_3PO_4 \cdot 9MoO_3$ (in the anhydrous form) or the same formula with 7 molecules of water in the hydrated form; the first of the proposed formulas corresponds to a cesium content of 22.3%; the second to 20.8%.

We see from the data submitted that the amount of cesium found does not correspond to the quantity of the latter in the trisubstituted salt of luteophosphomolybdic acid in question. The rubidium salt was not analyzed.

Our systematic study shows that the method of O'Leary and Papish cannot lead to luteophosphomolybdic acid without considerable contamination with the saturated heteropoly compound. Actually, on heating saturated phosphomolybdic acid to 300-350°, dehydration occurs as well as partial breakdown of the compound. The products of decomposition in this case are molybdic oxide and metaphosphoric acid.

During subsequent treatment with water, the remaining saturated phosphomolybdic acid naturally passes into solution together with the whole of the metaphosphoric acid which had been formed by breakdown of the complex, while the molybdenum oxide is precipitated.

The solution obtained after separation of the latter will contain free phosphoric acid. It was demonstrated that saturated phosphomolybdic acid in aqueous solution, in presence of phosphoric acid, partially changes into luteophosphomolybdic acid. This process took place also in the experiments of O'Leary and Papish who isolated a mixture of both acids and used it for determination of rubidium and cesium.

If O'Leary and Papish had made their observations on the basis of analytical results, they would have been convinced that the data obtained by them are in fairly good agreement with those calculated for the trisubstituted salt of saturated phosphomolybdic acid $Cs_3H_4[P(Mo_2O_7)_6] \cdot xH_2O$, which corresponds to a cesium content of 17.9% reckoned on the anhydrous composition of the salt. Evidently the cesium salt of saturated phosphomolybdic acid is less soluble than

the analogous salt of luteophosphomolybdic acid, and if both acids were present in the solution with whose help the precipitation was effected, then a salt of saturated phosphomolybdic acid would be precipitated.

The authors of the cited paper overlooked these facts. Although unable, in the absence of analyses of the prepared salts, to prove the value of the proposed method of determination of rubidium and cesium, they nevertheless ventured to recommend luteo-phosphomolybdic acid as a reagent for quantitative determination of rubidium and cesium.

EXPERIMENTAL

For the purpose of proving the erroneousess of the proposed procedure, we synthesized the rubidium and cesium salts of luteo- and saturated phosphomolybdic acids and determined their solubility in water at 25°.

P_2O_5 was determined by the pyrophosphate method under the conditions described by Rakovsky and Nikitina [4].

Water was determined by igniting a weighed amount of the salt to constant weight after preliminary drying at 100°.

For determination of Rb_2O and Cs_2O , the solution of salts was precipitated with quinoline hydrochloride [5]; after removal of the heteropoly anion, the filtrate was evaporated to dryness and ignited to constant weight; from the weight of chlorides obtained the amount of Rb_2O and Cs_2O was calculated.

Using the published method [3], preparation was first carried out of saturated phosphomolybdic acid in which the water and P_2O_5 were determined. Results of the analysis are set forth in Table 1. The MoO_3 content was found by difference.

TABLE 1

Analysis of saturated phosphomolybdic acid

Component of acid	Found (in %)	Calculated on anhydrous composition (in %)	Calculation from formula $P_2O_5 \cdot 24MoO_3$ (in %)
H_2O	12.88	—	—
P_2O_5	3.42	3.93	3.95
MoO_3	83.70	96.07	96.05

Addition of the prepared acid to a dilute (1%) rubidium chloride solution produced a pale-yellow precipitate which was filtered, washed until there was a negative reaction for chlorine ion in the wash liquor, and dried in the air.

The cesium salt of saturated phosphomolybdic acid was prepared in a similar manner. Both preparations were analyzed for their content of water and P_2O_5 ; the P_2O_5 content based on the anhydrous composition was (in %): for the rubidium salt 3.22, for the cesium salt 3.14.

The P_2O_5 content of the rubidium salt of saturated phosphomolybdic acid, calculated from the formula $3Rb_2O \cdot P_2O_5 \cdot 24MoO_3$ is 3.41%; that of the analogous cesium salt is 3.2%. Consequently we had prepared the trisubstituted salts of saturated phosphomolybdic acid.

The solubility of both salts in water at 25° was studied. The solubility of the rubidium salt was 0.021, and that of the cesium salt was 0.013%, i.e. these salts of saturated phosphomolybdic acid are sparingly soluble in water.

In addition we synthesized the rubidium and cesium salts of luteophosphomolybdic acid. They were isolated in the form of pale-yellow solids by adding an excess of saturated solution of luteophosphomolybdic acid to a nearly saturated solution of rubidium or cesium chloride.

The prepared salts were pressed, washed with iced water until free from chlorine ion (test on wash liquors), and analyzed for their content of water, P_2O_5 , Rb_2O and Cs_2O .

The MoO_3 content was found by difference.

The analytical results show that hexa-substituted salts of luteophosphomolybdic acid were obtained. The solubility of both salts in water at 25° was then determined. Withdrawal of samples for analysis of the liquid and solid phase was effected by the usually accepted methods. The content of Rb_2O and Cs_2O was determined in the solid phase; analysis confirmed that there was equilibrium between the liquid phase at the specified temperature and the same hexa-substituted rubidium and cesium salts of luteophosphomolybdic acid $Rb_6H_6[P_2O_7(Mo_2O_7)_3] \cdot xH_2O$ and $Cs_6H_6[P_2O_7(Mo_2O_7)_3] \cdot xH_2O$.

The results of the investigation are set forth in Table 3.

The determination of the solubility of the rubidium and cesium salts of luteo- and saturated phosphomolybdic acid in water at 25° showed that salts of saturated phosphomolybdic acid are slightly soluble; salts of luteophosphomolybdic acid are fairly soluble and cannot be used for analytical purposes; hence the results entirely refute the

TABLE 2

Analysis of cesium and rubidium salts of luteophosphomolybdic acid

Component of salt	Rubidium salt			Component of salt	Cesium salt		
	Found (in %)	Calculated on anhydrous composition	Calculated on hexa-substituted salt		Found	Calculated on anhydrous composition	Calculated on hexa-substituted salt
H ₂ O	11.13	—	—	H ₂ O	10.87	—	—
P ₂ O ₅	3.90	4.39	4.31	P ₂ O ₅	3.51	3.94	3.97
Rb ₂ O	15.24	17.15	17.02	Cs ₂ O	—21.14	23.72	23.62
MoO ₃	69.73	78.46	78.67	MoO ₃	—64.48	72.34	72.41

TABLE 3

Solubility of rubidium and cesium salts of luteophosphomolybdic acid in water at 25°

Salt of luteophosphomolybdic acid	Composition of liquid phase (grams of salt in 100 g solution)	Composition of crystal hydrate (in moles H ₂ O)
Rubidium	4.17	11.13
Cesium	5.08	10.87

recommended method of determination of rubidium and cesium. A suitable reagent for rubidium and cesium (in the absence of potassium) would be saturated phosphomolybdic acid since its rubidium and cesium salts are sparingly soluble.

SUMMARY

1. The hexa-substituted rubidium and cesium salts of luteophosphomolybdic acid were prepared.
2. The solubility in water of these salts at 25° was determined.
3. The solubility in water of the trisubstituted rubidium and cesium salts of saturated phosphomolybdic acid was determined; it was established that these salts are sparingly soluble.
4. It was shown that luteophosphomolybdic acid cannot be utilized as a reagent for quantitative determination of rubidium and cesium.
5. Saturated phosphomolybdic acid can serve, in the absence of potassium, as a reagent for rubidium and cesium.

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Received December 30, 1953

Institute of Chemical Reagents



INVESTIGATION OF THE TERNARY RECIPROCAL SYSTEM OF THE ADIAGONAL-BELT TYPE COMPOSED OF THE SULFATES AND MOLYBDATES OF LITHIUM AND POTASSIUM

A.G. Bergman, A.I. Kislova and E.I. Korobka

The ternary reciprocal system of the sulfates and molybdates of lithium and potassium is a part of the surface of crystallization of the quaternary reciprocal system of the sulfates and molybdates of lithium, potassium and sodium which we have studied.

EXPERIMENTAL

The investigation was carried out by the visual-polythermal method. The temperature of crystallization of the melts was determined in a platinum crucible with a Pt-Pt, Rh thermocouple and a galvanometer with a scale reading to 17 mV. The accuracy of the determination was 1-2°. The melts were stirred with a platinum stirrer. The sulfates used were chemically pure grades, twice recrystallized. The molybdates were prepared from ammonium paramolybdate and the respective carbonates. Our data for melting points of the molybdates agreed with the literature data. All the salts were thoroughly dehydrated, prior to use.

The binary systems (Table 1 and 3, Fig. 1) $\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4$, $\text{K}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$ and $\text{Li}_2\text{MoO}_4 - \text{K}_2\text{MoO}_4$, were previously investigated by Nacken and Amadori [1] and other authors. We repeated their determinations. Our results do not differ substantially from those of the earlier investigators. The system $\text{Li}_2\text{MoO}_4 - \text{Li}_2\text{SO}_4$, now studied by us for the first time, is a simple eutectic system.

A polymorphic transformation of lithium molybdate was detected at 630°. No clear indications of its existence appear in the literature [2]; in all cases, however, of investigation of both the binary systems and the cuts with participation of lithium molybdate, we clearly differentiated the change of phase at 630° accompanied by the appearance of a break on the curve.

The diagonal sections $\text{Li}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$ and $\text{Li}_2\text{SO}_4 - \text{K}_2\text{MoO}_4$ (Tables 1 and 3, Fig. 2) pass through the field of the complex compound $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$; hence they are not stable and do not participate in the triangulation of the system.

10 internal cuts were investigated in the reciprocal system (Tables 2 and 4, Figs. 3, 4 and 5). The presence was established of 8 fields of crystallization, the area of the square being apportioned as follows: fields of components - $\alpha\text{-Li}_2\text{SO}_4$ 2.44%, $\beta\text{-Li}_2\text{SO}_4$ 3.80%, $\alpha\text{-Li}_2\text{MoO}_4$ 2.99%, $\beta\text{-Li}_2\text{MoO}_4$ 18.46%, $\beta\text{-K}_2\text{SO}_4$ 0.81%; fields of compounds - $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ 23.38%, $\text{Li}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$ 6.77%; field of solid solutions $\text{K}_2[\text{MoO}_4, \alpha\text{-SO}_4]$ 43.35% (jointly with the fields of the components $\alpha\text{-K}_2\text{SO}_4$ and K_2MoO_4 - products of decomposition of the solid solutions). The greater part of the area of the square is occupied by fields of complex compounds.

The transverse-belt cut IV (Fig. 4), composed of the complex compounds $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ and $\text{Li}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$, located on opposite sides of the square of composition (Fig. 6), constitutes a simple eutectic system and divides the square of composition into two tetragons. The tetragons are subjected to a secondary triangulation by the sections extending from the vertices of the compounds to the vertex of the oppositely located component. The diagonals, however, as shown, do not participate in the triangulation; hence in the classification of Bergman and Bukhalova [3] the system belongs to the type of adiaagonal-belt systems. Such systems occur in cases when the reaction of exchange decomposition between the components of the system gives way to the reaction of formation of complex compounds at two opposite sides of the square of composition, i. e., in our system we have



The system contains three eutectic points and one transition point (Table 5).

The invariant points and the lines of common crystallization of the components and their compounds have been projected on to the side of the $\text{K}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$ square (Fig. 7). On the projection are also reflected the polymorphic transformations of the three components of the system: potassium sulfate at 596°, lithium sulfate at 574°, and lithium molybdate at 630° (straight lines).

TABLE 1

Sides and diagonal sections of the reciprocal system

Binary systems and diagonal sections	Starting component	Melting point of starting component	Component added	Crystallization branches and their points of intersection			
				Branch 1	Intersection of 1 and 2		Branch 2
					A*	B**	
$\text{Li}_2\text{MoO}_4 - \text{K}_2\text{MoO}_4$	Li_2MoO_4	705	K_2MoO_4	$\alpha - \text{Li}_2\text{MoO}_4$	14.5	630	$\beta - \text{Li}_2\text{MoO}_4$
$\text{Li}_2\text{MoO}_4 - \text{Li}_2\text{SO}_4$	Li_2MoO_4	705	Li_2SO_4	$\alpha - \text{Li}_2\text{MoO}_4$	35.5	630	$\beta - \text{Li}_2\text{MoO}_4$
$\text{K}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$	K_2MoO_4	924	K_2SO_4	$\text{K}_2[\text{MoO}_4, \alpha - \text{SO}_4]$	—	—	—
$\text{Li}_2\text{SO}_4 - \text{K}_2\text{SO}_4$	Li_2SO_4	858	K_2SO_4	$\alpha - \text{Li}_2\text{SO}_4$	12.5	574	$\beta - \text{Li}_2\text{SO}_4$
$\text{Li}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$	Li_2MoO_4	705	K_2SO_4	$\alpha - \text{Li}_2\text{MoO}_4$	11.5	630	$\beta - \text{Li}_2\text{MoO}_4$
$\text{Li}_2\text{SO}_4 - \text{K}_2\text{MoO}_4$	Li_2SO_4	858	K_2MoO_4	$\alpha - \text{Li}_2\text{SO}_4$	10	574	$\beta - \text{Li}_2\text{SO}_4$

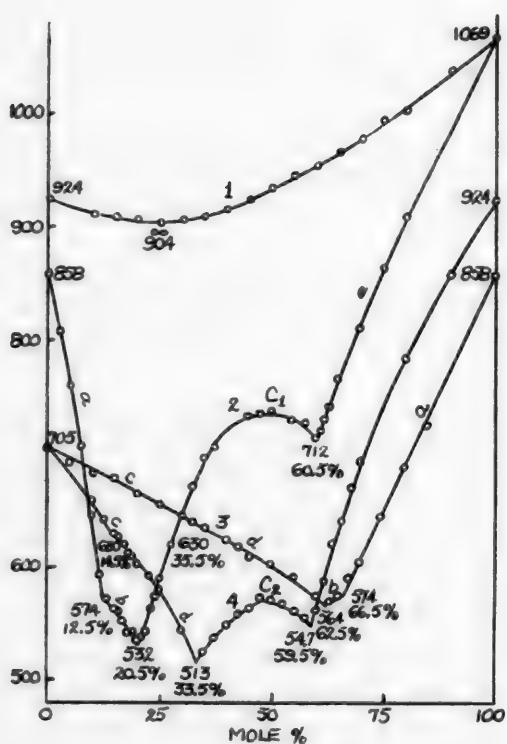


Fig. 1. Sides of the square of the reciprocal system.

1) $\text{K}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$, 2) K_2SO_4 , 3) $\text{Li}_2\text{MoO}_4 - \text{Li}_2\text{SO}_4$,
 4) $\text{Li}_2\text{MoO}_4 - \text{K}_2\text{MoO}_4$;
 a) $\alpha - \text{Li}_2\text{SO}_4$, b) $\beta - \text{Li}_2\text{SO}_4$, c) $\alpha - \text{Li}_2\text{MoO}_4$,
 d) $\beta - \text{Li}_2\text{MoO}_4$, e) $\alpha - \text{K}_2\text{SO}_4$;
 C₁ - $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, C₂ - $\text{Li}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$.

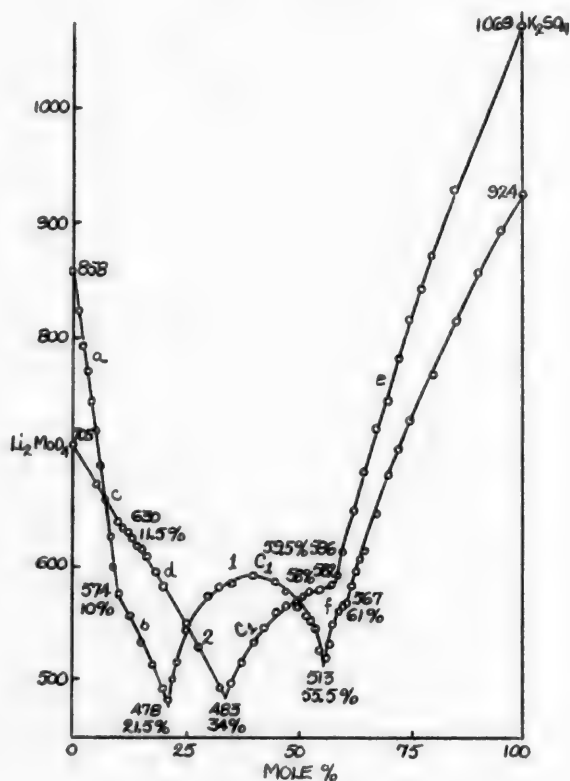


Fig. 2. Diagonal sections.

1) $\text{Li}_2\text{SO}_4 - \text{K}_2\text{MoO}_4$, 2) $\text{Li}_2\text{MoO}_4 - \text{K}_2\text{SO}_4$;
 a) $\alpha - \text{Li}_2\text{SO}_4$, b) $\beta - \text{Li}_2\text{SO}_4$, c) $\alpha - \text{Li}_2\text{MoO}_4$,
 d) $\beta - \text{Li}_2\text{MoO}_4$, e) $\alpha - \text{K}_2\text{SO}_4$, f) $\beta - \text{K}_2\text{SO}_4$;
 C₁ - $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$.

* Per cent of binary component
 ** Temperature

Table 1 continued

Crystallization branches and their points of intersection									Melting point			Fig. No.
Intersection of 2 and 3		Branch 3	Intersection of 3 and 4		Branch 4	Intersection of 4 and 5		Branch 5	of added component	of compound	eutectic	
A	B		A	B		A	B					
33.5	513	$\text{Li}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$	59.5	547	K_2MoO_4	—	—	—	924	569	513, 547	1
62.5	564	$\beta\text{-Li}_2\text{SO}_4$	66.5	574	$\alpha\text{-Li}_2\text{SO}_4$	—	—	—	858	—	564	
—	—	—	—	—	—	—	—	—	1069	—	—	
20.5	532	$\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$	60.5	712	$\alpha\text{-K}_2\text{SO}_4$	—	—	—	1069	736	532, 712	2
34	483	$\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$	58	582	$\beta\text{-K}_2\text{SO}_4$	59.5	596	$\alpha\text{-K}_2\text{SO}_4$	1069	—	—	
21.5	478	$\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$	55.5	513	$\beta\text{-K}_2\text{SO}_4$	61	567	K_2MoO_4	924	—	—	

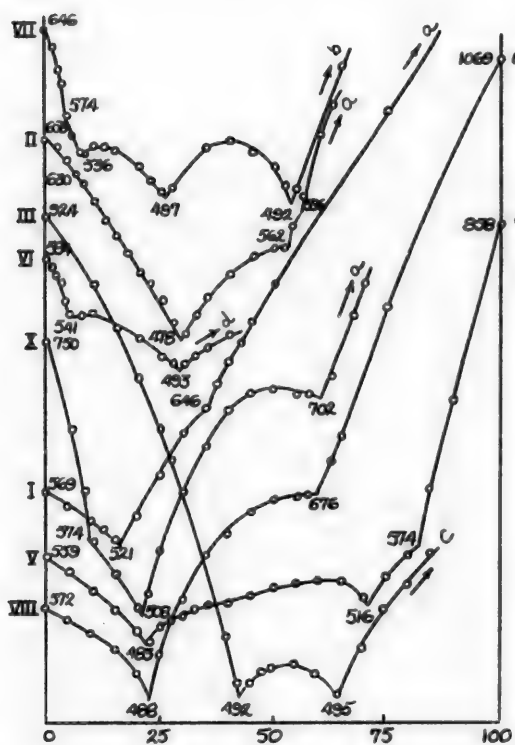


Fig. 3. Internal cuts in the directions:

→ a - K_2SO_4 → b - K_2MoO_4 → c - Li_2MoO_4 →
 → d - Li_2SO_4 .

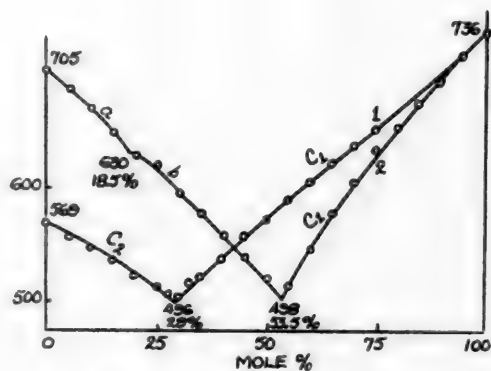


Fig. 4. Stable internal cuts.

1) IV, 2) IX.

a) $\alpha\text{-Li}_2\text{MoO}_4$, b) $\beta\text{-Li}_2\text{MoO}_4$;

C_1 - $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$, C_2 - $\text{Li}_2\text{MoO}_4 \cdot \text{K}_2\text{MoO}_4$.

TABLE 2

Internal cuts of the reciprocal system

Cut Number	Starting mixture of components (in %)	Melting point of starting mixture	Component added	Crystallization branches and their intersection points		
				Branch 1	Intersection of 1 and 2	
					A *	B **
I	50%K ₂ MoO ₄ + 50%Li ₂ MoO ₄	569	K ₂ SO ₄	Li ₂ MoO ₄ · K ₂ MoO ₄	16.5	521
II	90%Li ₂ MoO ₄ + 10%K ₂ MoO ₄	658	K ₂ SO ₄	a - Li ₂ MoO ₄	4.5	630
III	45%K ₂ SO ₄ + 55%K ₂ MoO ₄	924	Li ₂ MoO ₄	K ₂ [MoO ₄ · a - SO ₄]	43	492
IV	50%Li ₂ MoO ₄ + 50%K ₂ MoO ₄	569	Li ₂ SO ₄ · K ₂ SO ₄	Li ₂ MoO ₄ · K ₂ MoO ₄	29	496
V	45%K ₂ MoO ₄ + 55%Li ₂ MoO ₄	559	Li ₂ SO ₄	Li ₂ MoO ₄ · K ₂ MoO ₄	22	483
VI	62.5K ₂ MoO ₄ + 37.5Li ₂ MoO ₄	594	Li ₂ SO ₄	K ₂ [MoO ₄ · a - SO ₄]	5.5	541
VII	25%Li ₂ MoO ₄ + 75%Li ₂ SO ₄	646	K ₂ MoO ₄	a - Li ₂ SO ₄	3.5	574
VIII	40%Li ₂ MoO ₄ + 60%Li ₂ SO ₄	572	K ₂ SO ₄	a - Li ₂ MoO ₄	23	488
IX	50%Li ₂ SO ₄ + 50%K ₂ SO ₄	736	Li ₂ MoO ₄	Li ₂ SO ₄ · K ₂ SO ₄	53.5	498
X	12.5Li ₂ MoO ₄ + 87.5Li ₂ SO ₄	750	K ₂ SO ₄	a - Li ₂ SO ₄	8.5	574

TABLE 3

Temperature of start of crystallization of melts of binary systems and diagonal sections*

Binary systems						Diagonal sections					
Li ₂ SO ₄ - K ₂ SO ₄		K ₂ MoO ₄ - K ₂ SO ₄		Li ₂ MoO ₄ - K ₂ MoO ₄		Li ₂ MoO ₄ - Li ₂ SO ₄		Li ₂ MoO ₄ - K ₂ SO ₄		Li ₂ SO ₄ - K ₂ MoO ₄	
% K ₂ SO ₄	Tempe- rature	% K ₂ SO ₄	Tempe- rature	% K ₂ MoO ₄	Tempe- rature	% Li ₂ SO ₄	Tempe- rature	% K ₂ SO ₄	Tempe- rature	% K ₂ MoO ₄	Tempe- rature
5	760	10	912	10	658	10	682	5	671	5	718
10	645	20	906	12.5	641	20	664	10	638	9	598
12	592	25	903	15	628	25	654	12	628	12.5	556
13	572	35	909	18	611	35	632	15	615	21	484
15	561	45	924	20	602	40	622	25	549	22	500
19	540	50	933	25	578	50	599	32.5	494	25	542
21	536	60	954	30	543	60	572	35	497	35	585
25	588	70	978	35	523	63	566	40	533	40	591
35	694	75	993	40	546	65	572	50	569	45	585
45	732	80	1002	45	561	67.5	588	55	579	50	565
50	736	90	1038	50	569	75	642	57.5	582	55	526
55	728			55	559	80	687	59	592	56	519
60	713			60	559			60	612	58	549
61	720			64	619			70	743	60	565
70	810			70	691			75	814	62	582
75	864			80	783			85	924	75	727
80	908			90	859					90	855

* The number of experimental points is considerably reduced (Figs. 1 and 2).

** In the table are included the most important cuts. The number of points is cut down (Figs. 3 and 4).

Table 2 continued

Crystallization branches and their points of intersection										Fig. No.
Branch 2	Intersection of 2 and 3		Branch 3	Intersection of 3 and 4		Branch 4	Intersection of 4 and 5		Branch 5	
	A	B		A	B		A	B		
K ₂ MoO ₄	35.5	646	K ₂ SO ₄	—	—	—	—	—	—	3
α-Li ₂ MoO ₄	29	478	Li ₂ MoO ₄ · K ₂ MoO ₄	53	562	β-K ₂ SO ₄	55.5	596	α-K ₂ SO ₄	3
Li ₂ MoO ₄ · K ₂ MoO ₄	65.5	495	β-Li ₂ MoO ₄	—	—	—	—	—	—	3
Li ₂ SO ₄ · K ₂ SO ₄	—	—	—	—	—	—	—	—	—	4
β-Li ₂ MoO ₄	71.5	516	β-Li ₂ SO ₄	83	574	α-Li ₂ SO ₄	—	—	—	3
Li ₂ MoO ₄ · K ₂ MoO ₄	29	493	Li ₂ SO ₄ · K ₂ SO ₄	—	—	—	—	—	—	3
β-Li ₂ SO ₄	7	536	β-Li ₂ MoO ₄	26	497	LiSO ₄ · K ₂ SO ₄	53.5	492	K ₂ [MoO ₄ , α-SO ₄]	3
Li ₂ SO ₄ · K ₂ SO ₄	60	676	K ₂ [MoO ₄ , α-SO ₄]	—	—	—	—	—	—	3
β-Li ₂ MoO ₄	18.5	630	α-Li ₂ MoO ₄	—	—	—	—	—	—	4
β-Li ₂ SO ₄	21	508	Li ₂ SO ₄ · K ₂ SO ₄	60.5	702	K ₂ [MoO ₄ , α-SO ₄]	—	—	—	3

TABLE 4

Temperature of start of crystallization of melts of the internal cuts *

Cut I		Cut III		Cut IV		Cut V		Cut VII		Cut IX	
50% Li_2MoO_4 } 50% K_2MoO_4 } → K_2SO_4		45% K_2SO_4 } 55% K_2MoO_4 } → Li_2MoO_4		$Li_2MoO_4 \cdot K_2MoO_4$ → $Li_2SO_4 \cdot K_2SO_4$		45% K_2MoO_4 } 55% Li_2MoO_4 } → Li_2SO_4		25% Li_2MoO_4 } 75% Li_2SO_4 } → K_2MoO_4		Li_2MoO_4 → → $Li_2SO_4 \cdot K_2SO_4$	
% K_2SO_4	Temperature	% Li_2MoO_4	Temperature	% $Li_2SO_4 \cdot K_2SO_4$	Temperature	% Li_2SO_4	Temperature	% K_2MoO_4	Temperature	% $Li_2SO_4 \cdot K_2SO_4$	Temperature
5	556	10	864	10	546	5	546	1	632	5	688
10	543	20	780	15	536	10	529	3	599	10	671
15	526	25	737	25	510	20	493	4	569	15	649
20	549	35	622	30	503	22.5	484	5	553	20	629
25	585	40	549	35	519	25	497	8	536	30	595
30	622	42.5	507	45	558	30	507	10	543	40	556
35	645	45	507	50	572	35	516	15	540	50	516
37.5	668	50	520	60	605	45	526	25	503	55	510
42.5	705	55	523	70	638	55	536	27.5	507	60	543
50	756	60	516	75	652	65	539	35	543	65	576
75	914	65	497			70	523	40	549	75	632
		70	540			75	543	50	526	85	674
		80	599			80	562	52.5	510		
		85	625			85	623	55	507		
								65	616		

* In the table are included the most important cuts. The number of points is cut down (Figs. 3 and 4).

TABLE 5

Compositions and temperatures of the invariant points

Designations of points	Character of points	Temperature	Composition (in mole-%)				Equilibrium phases
			Li ₂ MoO ₄	K ₂ SO ₄	K ₂ MoO ₄	Li ₂ SO ₄	
E ₁	Eutectic	466	25.5	22.0	—	52.5	β-Li ₂ SO ₄ , Li ₂ SO ₄ · K ₂ SO ₄ , β-Li ₂ MoO ₄
E ₂		474	36.5	—	37.5	26.0	β-Li ₂ MoO ₄ , Li ₂ SO ₄ · K ₂ SO ₄ , Li ₂ MoO ₄ · K ₂ MoO ₄
E ₃		475	48.5	29.0	22.5	—	K ₂ MoO ₄ , Li ₂ SO ₄ · K ₂ SO ₄ , Li ₂ MoO ₄ · K ₂ MoO ₄
P	Transition	508	44.5	42.0	13.5	—	Li ₂ SO ₄ · K ₂ SO ₄ , K ₂ MoO ₄ , β-K ₂ SO ₄

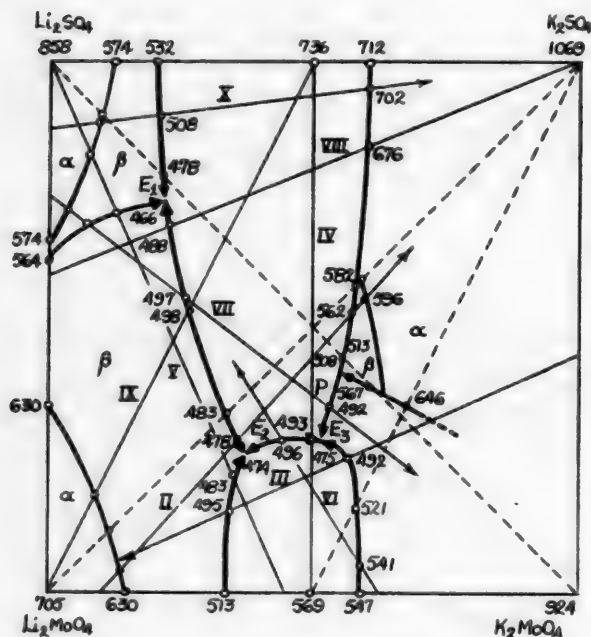


Fig. 5. Direction of internal cuts.

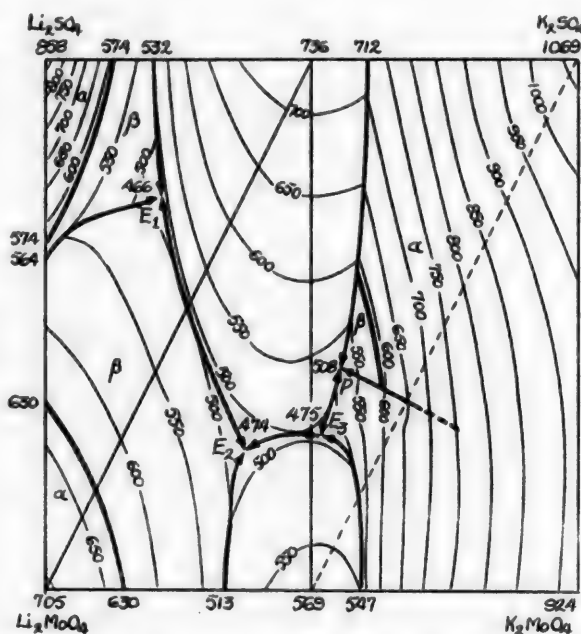
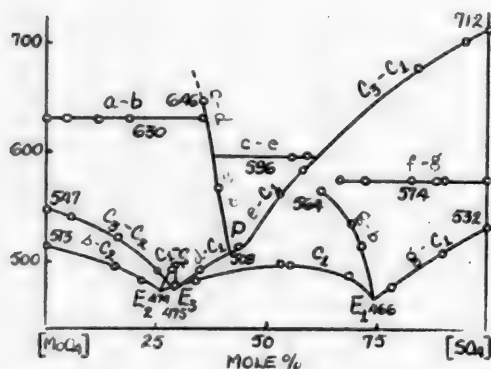


Fig. 6. Projection of the diagram of the reciprocal system on to the square of composition.

Fig. 7. Projection of the crystallization tree on to the K₂MoO₄ - K₂SO₄ side.

a) α-Li₂MoO₄, b) β-Li₂MoO₄, c) α-K₂SO₄, d) K₂MoO₄,
 e) β-K₂SO₄, f) Li₂SO₄, g) β-Li₂SO₄;
 C₁ - Li₂SO₄ · K₂SO₄, C₂ - Li₂MoO₄ · K₂MoO₄, C₃ -
 - K₂[MoO₄ · SO₄].

SUMMARY

1. The surface of crystallization of the ternary reciprocal system of the sulfates and molybdates of lithium and potassium was investigated by the visual-polythermal method.

2. For the first time a study was made of the binary system Li₂MoO₄ - Li₂SO₄, which constitutes a simple eutectic system with a eutectic point at 564° and 62.5% Li₂SO₄.

3. A special feature of the system is the formation of complex compounds at two opposite sides of the square: Li₂SO₄ · K₂SO₄ and Li₂MoO₄ · K₂MoO₄. The transverse, so-called "belt", section constituted by these complex compounds forms a simple eutectic system and is stable; it divides the square of composition into two tetragons. Further triangulation of the tetragons into simplex figures is effected by sections constituted by complex compounds and the oppositely

situated components. One of them, $\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4 - \text{Li}_2\text{MoO}_4$, is stable. On the basis of the foregoing observations, the system belongs to the eutectic type of adiaagonal-belt systems. Consequently the reaction of formation of complexes distributed over two opposing sides of the square predominates over the reaction of exchange decomposition.

The diagonal sections are not stable and do not participate in the triangulation of the system.

4. The solid solutions formed on the side of the square of compositions between the components $\alpha - \text{K}_2\text{SO}_4$ and K_2MoO_4 also extend inside the system, but with increasing content of the third component they become unstable and break down.

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Received February 3, 1954

Kuban Institute of Agriculture

• T. p. = C. B. Translation pagination.

EXPERIMENTAL DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE REACTION OF DECOMPOSITION OF MAGNESIUM HYDROXIDE

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In the literature on the decomposition of magnesium hydroxide and its thermodynamic characteristics there are no direct experimental data on the determination of the equilibrium constant of this reaction. The temperature dependence of the equilibrium constant is unknown; also, there is some discrepancy between the existing values of the thermal effect of the reaction. For example, according to the data of Fricke and Lücke [1] the heat of formation (Q_0) of magnesia from the hydroxide, determined calorimetrically from indirect data, ranges from 18.62 to 21.34 kcal; according to Johnston [2] the value is 13.10 kcal; according to Mixer [3] it is 9.4 kcal.

Thermochemical calculation on the basis of Hess' law, using existing tables of data [4, 5] ($\Delta H^0 \text{Mg(OH)}_2 = 218.7 \text{ kcal}$, $\Delta H^0 \text{MgO} = 146.1 \text{ kcal}$ and $\Delta H^0 \text{H}_2\text{O} = 57.8 \text{ kcal}$),* gives a value of 14.8 kcal.

In view of the contradictory character of existing literature data, it was of interest to undertake a direct experimental investigation of the equilibrium constant of the reaction of dehydration of magnesium hydroxide over a wide temperature range.

Dehydration of magnesium hydroxide is an endothermic process proceeding with separation of one product in the gas (vapor) phase: $\text{Mg(OH)}_2 = \text{MgO} + \text{H}_2\text{O (gas)}$.

Consequently the magnitude of the equilibrium constant in this case is governed by the equilibrium value of the fugacity of water vapor over a mixture of solid magnesia and magnesium hydroxide.

The apparatus selected for measurement of the equilibrium fugacity of the vapor consisted of a high-pressure bomb (volume 135 ml) placed in an electric furnace, and a pressure gage.

The set-up is illustrated in Fig. 1. In order to avoid condensation of water vapor in the inner chamber (Bourdon chamber) of the pressure gage, the latter was filled with water. The narrow connecting tube between the gage and the head of the bomb was likewise filled with water. A platinum-platinorhodium thermocouple was fixed to the body of the bomb for measurement of temperature. Magnesium hydroxide was prepared by treating magnesium sulfate with caustic alkali and washing the precipitate free from sulfate ions before drying to constant weight in a thermostat at 150°. The water content of the magnesium hydroxide was 30.9%, i.e., the theoretical amount. The experimental procedure was as follows. Small tablets of the prepared magnesium hydroxide were carefully screened to remove powdery hydroxide, which could choke the connecting tube (during measurements), and placed in the bomb. The amount charged into the bomb was 120 ml (about 60 g).

Before the start of the measurements, the whole apparatus was tested for tightness; then the electric furnace was switched on, and with the help of a transformer the necessary temperature was established; then the measurements were performed.

As special experiments at 450° showed, equilibrium pressure was established after 3 hours; at 500-650° it was established in 1.5-2 hours. The magnitudes of the equilibrium pressure at various temperatures are shown in the table.

The dependence of the equilibrium pressure on the temperature is plotted in Fig. 2.

Utilizing the isochoric equation

$$\frac{d \ln K_V}{dT} = \frac{-Q_V}{RT^2} \quad (1)$$

where K_V — is the equilibrium constant at constant volume; Q is the thermal effect of the reaction at constant volume we can determine the thermal effect of the reaction.

* ΔH^0 — is the change of heat content accompanying the reaction of formation of 1 mole of a given substance from the elements in their standard state.

Values of equilibrium pressure of water vapor in the decomposition of magnesium hydroxide at various temperatures

Temperature	Pressure ($P_{\text{atm.}}$)
380°	34
430	64
475	100
516	140
550	200
600	298
650	420

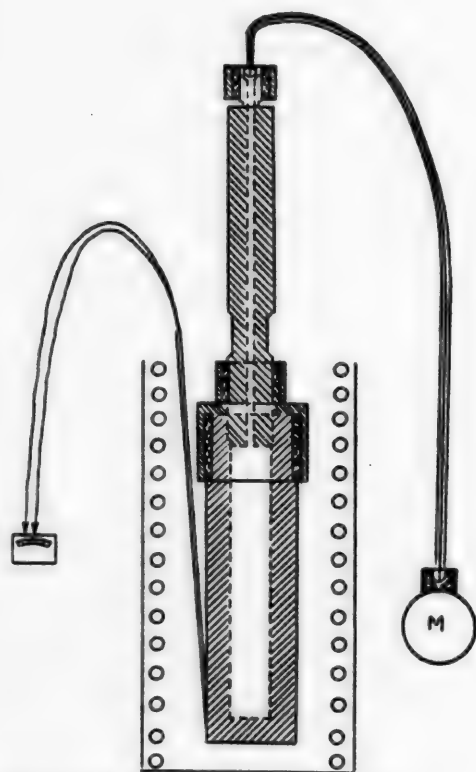


Fig. 1. Diagram of apparatus for determination of equilibrium pressure of water vapor

straight line, is 11,000 cal/mole, while B is 5.24. Equation (2) thus acquires the form:

$$\log K_v = \log P_{\text{equil.}} = \frac{11000}{4.575T} + 5.24. \quad (3)$$

SUMMARY

1. The equilibrium pressure and equilibrium constant of the decomposition of magnesium hydroxide in the temperature range of 380-650° were determined.

2. On the basis of experimental data and using the

For this purpose Equation (1) was taken in the integrated form:

$$\ln K_v = \ln P_{\text{equil.}} = \frac{Q_v}{RT} + B \quad (2)$$

As we see from Fig. 3, the dependence of the logarithm of the equilibrium pressure on the reciprocal of the temperature is well expressed by a straight line, indicating substantial constancy of Q_v over the range of temperatures studied.

The magnitude of the thermal effect, calculated from the tangent of the angle of slope of the

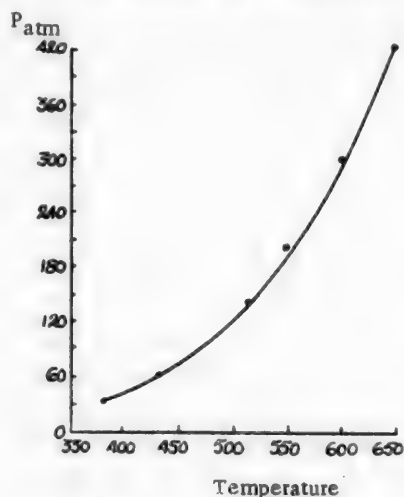


Fig. 2. Dependence of equilibrium pressure of water vapor during decomposition of magnesium hydroxide on the temperature.

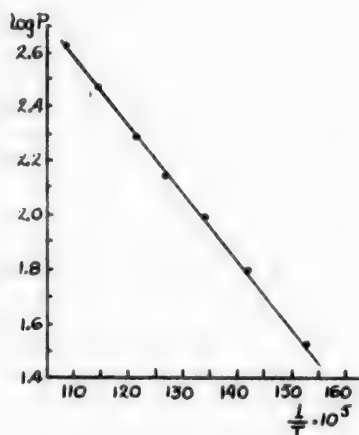


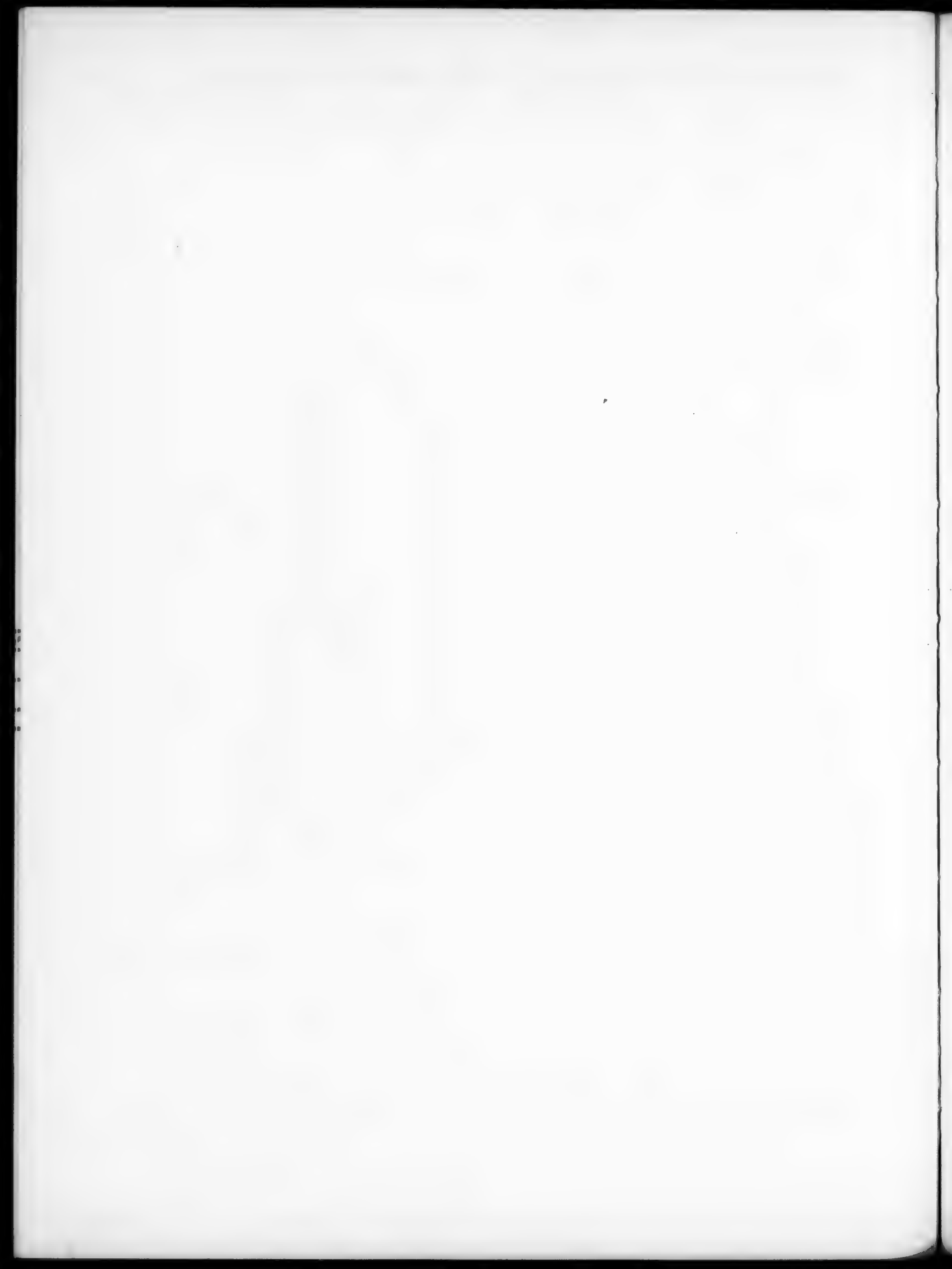
Fig. 3. Dependence of the logarithm of the equilibrium constant of the decomposition of magnesium hydroxide on the reciprocal of the temperature.

isochore equation, a value of 11,000 cal/ mole was found for the thermal effect of the reaction.

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Received January 9, 1954.



HETEROTRIACIDS

III. SILICOTUNGSTOVANADIC ACID

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Due to the formation in an acidic medium of the sparingly soluble tungstic acid, the synthesis of heteropoly acids containing tungsten proceeds with considerably greater difficulty than the preparation of analogous compounds of molybdenum.

This difficulty is eliminated by a number of authors [1] in the preparation of silicotungstic acid by preliminary conversion of the tungstate used for the synthesis into an acid-soluble paratungstate by careful neutralization with strong acids of the hot solution of the normal tungstate. The resultant reaction proceeds according to the equation:



It was quite natural to use this preparative method for the synthesis of silicotungstovanadic acid. Starting from the previously prepared sodium paratungstate, silicate and metavanadate, Gritskaya carried out a large number of experiments on the preparation of the heterotriacid by the etherate method, and a large number of factors bearing upon the process of separation of the compound concerned in the free state were investigated. With various ratios of starting substances in a weakly acid medium, with boiling, the solution in all cases had a yellow color. This distinguished it, above all, from the solutions that we obtained under similar conditions during preparation of all other heterotriacids containing vanadium, the color of which was bright-red.

In preparing the etherate from this yellow solution, a precipitate began to form even at an acidity of 0.8 N hydrochloric acid, and the size of the precipitate increased on supplementary addition of acid. In some experiments a small amount of colorless etherate was obtained, evidently silicotungstic acid. The $\text{V}_2\text{O}_5^{--}$ radical did not enter the complex ion. We also failed to obtain silicotungstovanadic acid by reaction under various conditions of excess of vanadate with prepared silicotungstic acid. However, a simple change in the procedure for the preparation, namely, neutralization of normal sodium tungstate with hydrochloric acid in presence of silicate (two-fold excess) under otherwise identical conditions, led to formation of a silicotungstovanadic complex which gave an etherate. On shaking this solution with ether in a hydrochloric acid medium (4 N) there was formed a relatively small quantity of yellow etherate from which, after its decomposition, could be isolated crystals of yellow color. Judging by the color of the crystals, vanadium was present in the form of the VO_3^{--} radical. Analysis showed that vanadium was present in extremely small amount, the ratio of V to W being 1:34. It is perfectly obvious that the introduction of vanadium under these conditions is only effected with great difficulty.

We carried out further investigations on the determination of the most favorable conditions for maximum introduction of vanadium into the complex ion of silicotungstovanadic acid of the saturated type. We were able to establish that the synthesis is successful if we start not from paratungstate but from a product containing anions of metatungstic acid.

Formation of anions of metatungstic acid from normal tungstate proceeds according to the equation:



On the basis of the equation, each gram of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ requires 2.3 g H_2WO_4 . In our experiments we gradually added to a boiling solution of normal sodium tungstate, with constant stirring, powdered tungstic acid until a small amount of acid remained unreacted under these conditions. The amount of the latter introduced was 1 g per gram of sodium tungstate, i.e., the above reaction did not proceed to completion. After filtration, addition was made to the resultant mixture, heated to boiling in a conical flask, of a hot mixture of solutions of sodium metavanadate (NaVO_3) and sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). The solution in the flask immediately turned an orange color. The contents of the flask were boiled with periodical addition of water so that the volume of liquid remained unchanged. A study of the influence of the duration of boiling on the course of synthesis showed that silicotungstovanadic acid may be formed after only 5-10 minutes' boiling, but in that case the yield of etherate is considerably reduced because formation of the latter is accompanied by precipitation of tungstic acid, which contaminates the etherate. Good results are obtained by boiling for $1\frac{1}{2}$ hours.

After boiling for the specified period, dropwise addition is made (without lifting the flask from the hot plate) of sufficient H_2SO_4 (1:1) to impart an acidity of 10-12 N H_2SO_4 . The contents of the flask are then cooled under the tap and transferred to a separating funnel; ether is added and the mixture shaken. The resultant drops of orange-colored etherate fall to the bottom of the funnel. More complete separation of etherate can be achieved if toward the end of the shaking a further small amount of H_2SO_4 (1:1) is introduced. The separated etherate is washed with 10 N H_2SO_4 saturated with ether, and after thorough cooling it is placed in a shallow crystallizing dish. The etherate is decomposed by addition of water until "boiling-up" ceases. The residual ether is driven off by careful heating in water at 60-70°. On standing for about 24 hours, orange crystals of silicotungstovanadic acid are formed and are separated from mother liquor by filtration through a funnel with a porous base before drying on a watch glass at room temperature.

In some of our preparative experiments we took the following amounts of starting substances: $\text{N}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ - 16.5 g; NaVO_3 - 5.8 g; and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ - 2.8 g. These amounts were calculated from the ratio $\text{Si} : \text{W} : \text{V} = 1 : 10 : 4$, i.e. the amount of vanadate was twice as large as is required by the formula $\text{H}_8[\text{Si}(\text{W}_2\text{O}_7)_5\text{V}_2\text{O}_6]$. The optimum volume of solution in which the complex was prepared by boiling was 50-60 ml. At higher dilutions the yield of etherate decreases. Prior to the boiling, 2 ml H_2SO_4 (1:1) was added, and after 1 1/2 hours 75 ml was added. The yield of product was 70% of the theoretical.

Analysis. The water of crystallization in the synthesized compound was determined by drying and by the hydride method.

Silicon was determined from the loss in weight of the sum of the oxides after working up with hydrofluoric acid under the previously described conditions [2].

For determination of vanadium and tungsten, a weighed amount of the heterotriacid of the order of 0.7-g was dissolved in a 100 ml measuring flask.

The vanadium was determined in 10 ml of the prepared solution after decomposing the silicotungstovanadic complex with 25 ml of a mixture of equal volumes of H_2SO_4 (d 1.84), H_3PO_4 (d 1.7) and water. Heating was carried out until the solution had acquired a blue color. Water was then added to make up the volume to 50 ml and titration was performed with Mohr's salt in presence of phenylanthranilic acid until the blue-violet color disappeared.

In another aliquot portion (10 ml) of the solution was determined the sum of tungsten and vanadium. This was done by transferring the solution to a funnel of 200 ml capacity fitted with a bottom ground-glass tap and a side tap (also ground-glass) situated one-third of the way down from the stopper. The side tube was connected to a 10 ml receiver filled with freshly boiled water saturated with carbon dioxide. Into the funnel was introduced 10 ml lead amalgam and 40 ml HCl (d 1.19); it was then heated in a beaker containing hot water (80-90°), the funnel being arranged with the open stopper on its side so that it was supported by the walls of the beaker. Heating was carried out for 5-10 minutes, and then carbon dioxide was passed in through the side tap from a Kipp's apparatus (with half-opened tap) and the funnel was vigorously shaken (10-15 minutes) until the solution had a khaki color. After reduction of the tungsten to the trivalent and vanadium to the pentavalent form, the amalgam was transferred to the receiver, and the solution into a twofold excess of standard 0.05 N potassium bichromate solution, the lead from the Kipp's apparatus having been connected to the side tap of the funnel and the lower tap of the funnel to a glass tube extending to the bottom of the vessel containing the bichromate solution. In this way the vanadium was oxidized to the tetravalent form and the tungsten to the hexavalent form which was precipitated as tungstic acid. The excess of bichromate was titrated with thiosulfate solution in presence of 0.2 g potassium iodide and starch until appearance of a grey-green color (with a yellow tinge).

Knowing the total of tungsten and vanadium and the amount of vanadium separately, the tungsten could be calculated by difference.

In the following table are set forth the results of analysis of three specimens of synthesized heterotriacid. For the sake of brevity we only give the weights taken for determination of the silica content; the content of the other components and of water of crystallization was calculated from these weights.

Products obtained by utilizing paratungstate and metatungstate as starting substances are readily soluble in water, and in presence of inorganic acids they do not form a precipitate of tungstic acid.

Treatment with 5% solution of o-hydroxyquinoline in acetic acid brings down yellow precipitates even at an acidity reaching 1.3 N HCl, whereas, from the separately taken sodium vanadate and sodium tungstate, vanadium comes down at an acidity not exceeding 0.001 N and tungsten at an acidity not exceeding 10^{-5} N. Analysis of the precipitates obtained in a hydrochloric acid medium showed that the ratios of $\text{SiO}_2 : \text{WO}_3 : \text{V}_2\text{O}_5$ scarcely differed from the ratios found for aqueous solutions of the heterotriacids in question, as seen from Table 2 in which are set forth the mean values of the three analyses.

TABLE 1

Results of analysis of silicotungstovanadic acid

Specimen Number	Weight (in g)	SiO ₂		WO ₃		V ₂ O ₅		H ₂ O		Ratio SiO ₂ : WO ₃ : V ₂ O ₅ : H ₂ O
		(g)	(mole)	(g)	(mole)	(g)	(mole)	(g)	(mole)	
1	0.779	0.0135	0.00022	0.550	0.00237	0.041	0.00022	0.102	0.00566	1 : 10.8 : 1 : 26
2	0.771	0.012	0.00022	0.498	0.00215	0.042	0.00023	0.140	0.00777	1 : 9.8 : 1.1 : 35
3	0.854	0.015	0.00024	0.548	0.00237	0.056	0.00031	0.159	0.00883	1 : 9.9 : 1.3 : 37

TABLE 2

Heterotriacid	Analysis of solution	Analysis of precipitate from o-hydroxyquinoline
	SiO ₂ : WO ₃ : V ₂ O ₅	SiO ₂ : WO ₃ : V ₂ O ₅
Prepared from paratungstate	1 : 34 : 0.5	1 : 3.6 : 0.5
Prepared from metatungstate	1 : 10.2 : 1	1 : 10.1 : 0.98

EVALUATION OF RESULTS

All our studies of the synthesis of silicotungstovanadic acid showed that the decisive factor in the formation of the heteroion of the given compound is the nature of the tungstate anion used as starting substance. During formation of silicotungstic acid, the transition of normal tungstate into paratungstate

is not accompanied by formation of precipitated tungstic acid in the process of formation of the etherate, whereas this effect does not arise in the present case. The silicotungstovanadic acid separated by employing paratungstate differs sharply from other vanadic heterotriacids synthesized by us by virtue of its color and its very low content of vanadium; evidently it belongs to another series of compounds. The tendency to crystallize and the precipitating action of o-hydroxyquinoline indicate that it is an individual substance.

An entirely different result is obtained on synthesis after preliminary conversion of tungstate into metatungstate. Tungstic acid is then not precipitated during formation of the etherate. Introduction of vanadium proceeds without special difficulties. The resultant compound is bright-red, justifying the conclusion that the $V_2O_6^{--}$ radical was introduced. Analyses of three samples of synthesized products show that they are all heterotriacids of the saturated type - $H_8[Si(W_2O_7)_5V_2O_6] \cdot nH_2O$. Slight deviations in the ratio of $WO_3 : V_2O_5 = 10 : 1$ are clearly explained by the difficulty of accurate determination of small amounts of vanadium in presence of a large content of tungsten.

The great difference between the crystal water content of the first specimen on the one hand and the second and third specimens on the other is accounted for by the conditions of crystallization; observations show that the slower the crystallization the higher the crystal water content of the hydrates.

SUMMARY

1. Conditions were established for the synthesis by the etherate method, and silicotungstovanadic acid was isolated in the crystalline form.
2. It is shown that the decisive factor for synthesis of this acid is previous conversion of normal tungstate into metatungstate.
3. Determination of the composition of the heterotriacid indicated that it may be represented by the formula $H_8[Si(W_2O_7)_5V_2O_6] \cdot nH_2O$, where $n = 26 - 37$.

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Received August 24, 1953

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STUDY OF THE REACTIONS OF POLYTHIONATES WITH THE HELP OF LABELED SULFUR

I. REACTION OF TRITHIONATES

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Many studies have been devoted to the reactions of formation and decomposition of polythionates. The complex processes of their transformations with participation of sulfides, sulfites, thiosulfates and elemental sulfur are not easily amenable to study by the usual chemical methods. Up to now their study has been limited to the determination of the composition of the reacting mixtures, to its change with time and to the isolation of the products formed. These data do not permit us to draw decisive conclusions, as can be seen from the abundance of diverse and contradictory concepts of the course and intermediate steps of these reactions.

The application of isotopic methods is bound to introduce greater clarity into this problem. Up to the time of commencement of our research, only one investigation had been published [1] on the decomposition of tetrathionate with sulfite using labeled sulfur. In 1952-1953 other papers appeared which used this method for studying the reactions of decomposition of tetrathionate with sulfide and with mercuric chloride [2], the decomposition of polythionates with caustic alkali [3], and the formation of sulfur in the Wackenroder reaction [4].

Below are presented the results of a study of the mechanism of reactions of formation of trithionate with the help of radiosulfur.

EXPERIMENTAL

Decomposition of trithionate. Potassium trithionate was prepared by the three methods described below from compounds containing radiosulfur in specific positions. For establishment of their position in the prepared trithionate, the latter was decomposed by boiling with potassium carbonate solution according to the over-all reaction:



The distribution of activity in the thiosulfate was found by converting the latter into the silver salt, which was decomposed by boiling with water:



From previous studies [5, 6] it is known that in this process the outer (sulfide) atom of sulfur of the thiosulfate passes into silver sulfide and the inner (sulfite) atom into sulfuric acid, and also that there is no exchange between both atoms of sulfur either in the thiosulfate itself or in the process of its decomposition. We confirmed this both by special experiments and by the data of Tables 1 and 5 in which the whole activity of the original sulfur passes into the final silver sulfide.

The sulfate resulting from decomposition of the trithionate was precipitated with strontium nitrate. In the first experiments considerable error was introduced due to part of the sulfate remaining in solution and then changing into thiosulfate. In the final experiments the residue of sulfate, following precipitation with SrSO_4 , was removed from the filtrate by careful addition of BaCl_2 until cloudiness no longer appeared. After this, the thiosulfate was precipitated with excess of BaCl_2 . The precipitated barium thiosulfate was washed with alcohol and dried. A weighed amount of the barium thiosulfate was then dissolved in hot water and converted into sodium thiosulfate by addition of the calculated amount of sodium sulfate. After this the thiosulfate was perfectly pure. All the described operations do not lead to change of the isotopic content since the sulfates do not exchange sulfur with sulfites, thiosulfates [6, 7] and trithionates. We failed to detect any exchange with the latter at 25° after 26 hours.

Measurement of activity. In the first experiments the activity of the precipitates was measured directly; this led to poor reproducibility. In the final experiments the activity of the sulfate resulting from decomposition of trithionate was measured in the form of SrSO_4 , while that of all the remaining compounds and of elemental sulfur was measured in the form of benzidine sulfate after Carius oxidation. For this purpose, an ampoule containing 15 mg sample, 15 mg NaBr and 0.2 mg conc. HNO_3 was heated 1 hour at 300°; the contents of the ampoule were then dissolved in water and evaporated on a water bath, and the residue dissolved in 10 ml water and 6 ml alcohol. The

solution was precipitated with the calculated amount of benzidine chloride solution (5 g in 40 ml 1 N HCl with addition of 50% alcohol to a volume of 250 ml). The precipitate was washed on the filter and dried; 4 mg precipitate was spread out on a small circle of filter paper on a plexiglas support which was then pushed into the groove of a stand fitted with a counter-tube. The reproducibility of the measurements was approximately 2-4%. In the tables are set forth the number of impulses above the background in 5 minutes, calculated for 1 mg sulfur. If the number of impulses above the background did not exceed 30 (for a total number of 3,000-15,000), the activity was considered zero.

Trithionate from sulfur dichloride and bisulfite. Chlorination of active sulfur was undertaken at 200-250°. To the resultant S_2Cl_2 was added a little sulfur, and it was purified by distillation. The 137-138° fraction with addition of 1% carbon was chlorinated at 0°. The excess chlorine was removed by blowing CO_2 through. The trithionate was prepared by the procedure of Stamm and Goehring [8]. SO_2 was passed with cooling into a solution of 16 ml 5 N KOH until the reaction was neutral. To this solution was added in small portions a solution of 2 g active SCl_2 in 30 ml ligroine. Cooled solutions were employed, and during the reaction the temperature did not rise above 10°. At the end of the reaction and on cooling to 0°, the precipitated potassium trithionate was recrystallized from water, washed with alcohol and then with ether, and dried in the air. It did not give reactions for Cl^- , SO_3^{--} , SO_4^{--} and higher polythionates.

Results of two experiments on the preparation and decomposition of trithionate are set forth in Table 1. Decomposition of the individual samples was performed twice. As seen from a comparison in Table 2, the activity of the trithionate was $1/3$ of that of the original sulfur. Its decomposition does not give active sulfate and thiosulfate in which the sulfide sulfur is inactive, but the sulfide sulfur has the same activity as the original sulfur. If the latter is assumed to be unity, then the data obtained exactly correspond to the scheme:

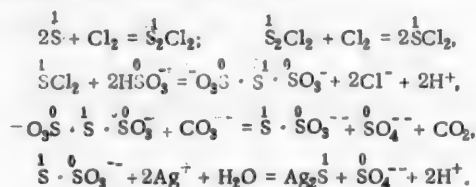


TABLE 1

Trithionate from $SCl_2 + HSO_3^-$

Experiment Number	Activity (impulses in 5 minutes per mg S)						
	Original S (A)	S_2Cl_2 (B ₁)	SCl_2 (B)	Trithionate (C)	Sulfate from trithionate (E)	Ag_2S from final thiosulfate (F)	Sulfate from final thiosulfate (G)
Experiment 1a } Experiment 1b }	1705	1700	1675	570	0	1660 1695	0 0
Experiment 2a } Experiment 2b }	2840	2795	2825	970	0	2735 2765	0 0

TABLE 2

Trithionate from $SCl_2 + HSO_3^-$

Experiment Number	Ratio of activities			
	A/B	A/C	A/F	F/C
Experiment 1a } Experiment 1b }	1.02	2.99	1.03 1.01	2.91 2.98
Experiment 2a } Experiment 2b }	1.01	2.93	1.04 1.03	2.82 2.85
Taken				
	1	3	1	3

Trithionate from thiosulfate and sulfur dioxide.

For preparation of $Na_2\overset{1}{S} \cdot \overset{0}{SO}_3$ with labeled sulfur in an external position, a solution of 20 g KOH in 40 ml water was saturated with SO_2 to a weakly acidic reaction, and then the same amount of KOH solution was added. The sulfite content was determined iodometrically. Into the solution was introduced the equivalent amount of pulverized active sulfur which dissolved completely on heating. Traces of SO_3^{--} and SO_4^{--} were precipitated with strontium nitrate and then with a few drops of barium chloride solution. The solution was evaporated up to a precipitation of the thiosulfate which was recrystallized, washed with alcohol and ether, and dried.

TABLE 3

Trithionate from $\overset{\bullet}{S} \cdot SO_3^{--} + SO_2$

Experiment Number	Activity (impulses in 5 minutes per 1 mg S)					
	Original S (A)	Original $Na_2S_2O_3$ (B)	Trithionate (C)	Sulfate from trithionate (E)	Ag_2S from final thiosulfate (F*)	Sulfate from final thiosulfate (G)
Experiment 1a } Experiment 1b }	4390	2215	1070	0	3095	-40
				-60	3325	0
Experiment 2a } Experiment 2b }	8320	4115	2090	0	6270	0
				0	6325	0
Experiment 3a } Experiment 3b }	4545	2160	1140	0	(2575)	0
				0	(2550)	0
Experiment 4a } Experiment 4b }	11880	5930	2865	0	8665	0
				30	8715	0
Experiment 5	16600	8295	4170	0	12290	0
Experiment 6	5820	2960	1415	0	4290	0

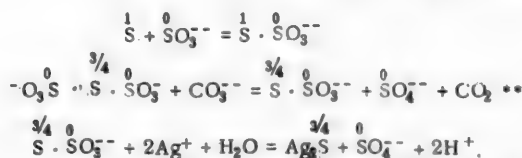
TABLE 4

Trithionate from $\overset{\bullet}{S} \cdot SO_3^{--} + SO_2$

Experiment Number	Ratio of activities			
	A/B	A/C	A/F	F/C
Experiment { 1a 1b }	1.98	4.10	1.42	2.89
			1.32	3.11
Experiment { 2a 2b }	2.02	3.98	1.33	3.00
			1.31	3.03
Experiment 3	2.10	3.98		
Experiment { 4a 4b }	2.00	4.15	1.37	3.02
			1.36	3.04
Experiment 5	2.00	3.98	1.35	2.95
Experiment 6	1.97	3.92	1.29	3.03
Taken				
	2	4	4/3	3

Trithionate was prepared [9] by passing a strong stream of SO_2 for $1\frac{1}{2}$ hours into a mixture of 0.4 ml saturated SO_2 solution and 2 g solid active thiosulfate with 1 drop of saturated arsenous acid solution. After separation of the precipitated tetrathionate, SO_2 was again passed through and the solution afterwards poured into a solution of 1 g potassium acetate in 1.2 ml water. The precipitated trithionate was purified as described above.

In a series of preliminary experiments, details of which are not given, not all the precautions were observed which ensure freedom of the tested precipitates from impurities. They gave qualitatively the same results as the final precise experiments set forth in Tables 3 and 4. The trithionate has $\frac{1}{4}$ the activity of the original sulfur. Its decomposition gives inactive sulfate and thiosulfate containing $\frac{3}{4}$ of the activity of the original sulfur. Decomposition of the latter gave inactive sulfate and Ag_2S containing $\frac{3}{4}$ of the activity of the original sulfur:



Trithionate from thiosulfate and hydrogen peroxide. The method of Willstätter [10] with some modifications was employed. To a solution of 3 g labeled $Na_2S \cdot SO_3$ in 2.5 ml water was added dropwise with cooling 30% hydrogen peroxide until the alkaline reaction to phenolphthalein had disappeared. With intense cooling a larger proportion of the sulfate came down. The remainder was precipitated by cautious addition of $BaCl_2$ solution. The trithionate was brought down by running in a solution of potassium acetate, and it was purified as described above.

* The $Na_2S_2O_3$ isolated from decomposition of trithionate gave in experiments 4, 5 and 6 impulses of 4325, 6165 and 2155.

** The degree of formation of trithionate is considered below.

TABLE 5

Trithionate from $\dot{S} \cdot SO_3^{--} + H_2O_2$

Experiment Number	Activity (impulses in 5 minutes per 1 mg S)						
	Original S (A)	Original $Na_2S_2O_3$ (B)	Trithionate** (C)	Sulfate from trithionate (E)	Final $Na_2S_2O_3$ (J)	Ag_2S from final thiosulfate (F)	Sulfate from final thiosulfate (G)
Experiment 1	5330	—	—	1390	—	5225	1225
Experiment 2a } Experiment 2b }	5130	2380	2370	1315 1255	— —	4380 4380	1070 1065
Experiment 3a } Experiment 3b }	2910	1420	1450	860* 880*	— —	2800 2880	625 660
Experiment 4a } Experiment 4b }	6740	3305	3340	1645 1650	3785 3865	6480 6560	1620 1585

As we see from Tables 5 and 6, both the trithionate and the simultaneously formed sulfate possessed $1/2$ the activity of the original sulfur. Decomposition of the trithionate gave silver sulfide with the activity of the original sulfur and sulfate with $1/4$ its activity. This is represented by the scheme:

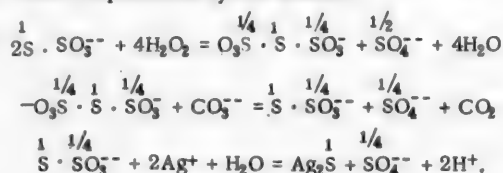


TABLE 6

Trithionate from $\dot{S} \cdot SO_3^{--} + H_2O_2$

Experiment Number	Ratio of activities						
	A/B	A/C	A/F	A/E	F/G	J/C	J/G
Experiment 1	—	—	1.02	3.83	4.27	—	—
Experiment 2a } Experiment 2b }	2.16	2.16	1.17 1.17	3.90 4.09	4.09 4.11	— —	— —
Experiment 3a } Experiment 3b }	2.05	2.01	1.04 1.01	(3.38)* (3.31)	(4.47)* (4.36)	— —	— —
Experiment 4a } Experiment 4b }	2.04	2.02	1.04 1.03	4.10 4.08	4.00 4.14	1.13 1.16	2.34 2.44
Taken							
	2	2	1	4	4	5/4	5/2

For an unknown reason the activity of sulfate E and G in experiments 1 and 3 differed by 10-20% from the corresponding scheme, but comparison with it of the activity of the remaining substances leaves no doubt about its correctness. In particular, in experiment 4 the final thiosulfate was isolated before hydrolysis and its activity was 1.15 times greater than the activity of trithionate and 2.4 times greater than the activity of sulfate G, whereas the scheme requires ratios of $5/4$ and $5/2$.

EVALUATION OF RESULTS

Before going on to consider the mechanism of the reactions corresponding to the determined distribution of activities, we must consider to what degree the distribution may be influenced by secondary exchange of sulfur.

In all cases the mean activity of the trithionate corresponds to the activity of the products of its decomposition—silver sulfide and sulfuric acid. All these activities are in simple ratios to one another and to the activity of the original sulfur. Furthermore, if the sulfate resulting from decomposition of trithionate had been inactive, then the final sulfate should also be inactive (Tables 1 and 3). All this excludes the possibility of alteration of the isotopic composition in the process of decomposition of trithionate due to exchange of sulfur. This is explained by the fact that the

* The separated sulfate evidently contained impurities.

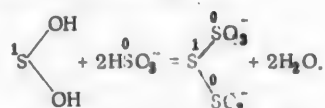
** The separated sulfate, formed at the same time as the trithionate, was contaminated with impurities. In experiments 1, 2, 3, and 4 it had activities of 1825, 1845, 1450 and 2950.

thiosulfate group enters the trithionate and is cleaved off from it without breaking down. Further evidence of this process is adduced below. These conclusions are directly confirmed by the results of a new investigation by Fava [11] which came to our notice only after the conclusion of the present work. Fava found that thiosulfate exchanges thionate sulfur with the middle sulfur of trithionate with a half-life of 12 hours at 25° and that the other atoms of sulfur of both compounds do not participate in the exchange. The same conclusion was also reached by other authors [1]. Consequently the distribution of active sulfur in trithionate proposed in the schemes can be regarded as correct.

The formation of trithionate by reaction of sulfur dichloride with bisulfite was predicted in 1870 by D. I. Mendeleev [12] and 3 years later was realized by Spring, but it has only recently [8, 13] been studied closely. Its mechanism is not in doubt. Sulfur dichloride is the anhydride of sulfoxylic acid which it forms on hydrolysis:



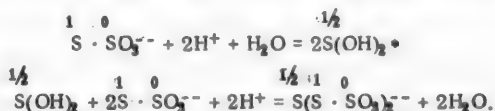
following which the hydroxyl groups are replaced by sulfite groups:



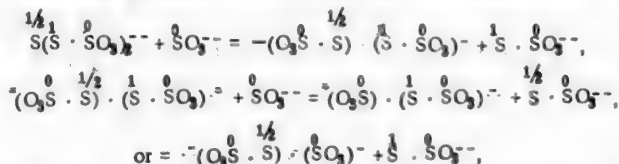
This simple mechanism, already put forward by other authors [8, 13], is directly confirmed by the data of Tables 1 and 2. It is in accord with the ideas of D.I. Mendeleev who regarded the polythionic acids as disulfonic acids formed by substitution of the hydrogen in hydrogen sulfides by sulfite groups, for example $\text{SH}_2 \rightarrow \text{S}(\text{SO}_3\text{H})_2$.

The reaction of sulfites with thiosulfates, as also the analogous reactions in Wackenroder liquid ($\text{H}_2\text{S} + \text{H}_2\text{SO}_3$), have been the subject of many investigations in which diverse mechanisms have been advanced. In the majority of contemporary studies the primary formation of sulfur monoxide SO or its hydrate (sulfoxylic acid) is suggested. Further reaction of the latter with sulfites and thiosulfates gives polythionates. An alternative theory is the initial formation of thiosulfurous acid [14, 15], or of hydrogen sulfoxide H_2SO [16]. It has also been suggested that the polythionates primarily formed are trithionate [17], tetrathionate [18, 19, 20], or pentathionate [16, 21], or simultaneously tri- and pentathionate [15, 22], or, finally, tetra- and hexathionate [14]. Equally diverse and conflicting are the equations proposed for these reactions and their steps.

From our results it follows that trithionate is not the primary product of reaction of sulfite with sulfur dioxide, because the central sulfur in trithionate has an activity different from that in all positions in the starting substances. A study of this reaction by chemical methods in presence of As_2O_3 revealed [23] that pentathionate is formed at first and later changes into tetra- and trithionate. Both can be isolated from the reaction mixture in good yield. The distribution of activities that we found exactly corresponds to the following scheme, which is also consistent with the chemical data. The primary product is sulfoxylic acid. Substitution of the hydroxyls in the latter by thiosulfate groups gives pentathionate:



Successive substitution of thiosulfate groups by sulfite groups gives tetrathionate and trithionate:



since in tetrathionate both thiosulfate groups are equivalent. In accord with experiments, both routes lead to the mean distribution:



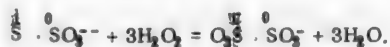
Isotopic exchange of sulfur between thiosulfate and both the higher polythionates only proceeds by exchange of the whole sulfite or thiosulfate groups. It is easy to see that it can influence the distribution of activity in the trithionate only in the event that the latter stage of its formation has a velocity of the same order as that of the first step of formation of pentathionate, since only in this latter stage does the thiosulfate possess an isotopic composition different

* The formation, suggested in some papers by Foerster, of SO or $\text{S}(\text{OH})_2$ from HSO_3^- or from $\text{H}_2\text{SO}_3 + \text{H}_2\text{S}_2\text{O}_3$ is inconsistent with our observations of the distribution of active sulfur.

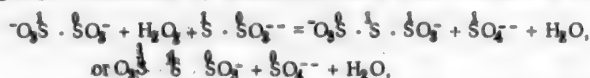
from that in the initial step, and it is mixed with the unreacted residue of the latter. The experimentally determined distribution of activity does not reveal an alteration of isotopic composition owing to exchange, evidently the consequence of the great difference in velocities of the two steps in question.*

It should be noted that the primary formation (suggested by other authors) of thiosulfurous acid, which gives tetrathionate [14], or of trithionate from sulfoxylic acid and sulfite [17, 15], or, finally, primary formation of H_2SO [16], are all inconsistent with our data.

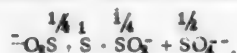
In the formation of trithionate from thiosulfate and hydrogen peroxide, in contrast to the two preceding cases, the sulfite (outer) sulfur of trithionate is likewise active. This activity could only be the result of intermediate oxidation of the labeled thionate sulfur of the original thiosulfate to sulfite sulfur. Evidently the only acceptable explanation of our observed distribution of activity is the oxidation of thiosulfate to an ion of a symmetrical acid with two atoms of sulfur — probably dithionic acid:



In the next step the sulfite group is substituted by thiosulfate and is itself oxidized to sulfate:

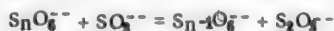


since exchange of both sulfite groups is equally probable. On the average this gives the observed distribution:



Formally this scheme also satisfies the intermediate formation of persulfate $\overset{1}{\text{O}_3\text{S}} \cdot \overset{1}{\text{SO}_4^-}$. Formation of dithionate at the same time as that of trithionate was detected during the Wackenroder reaction in studies by Zilberman [24], although in the latter papers it was attributed to a side reaction of oxidation of sulfite by the analog of hydrogen peroxide— H_2SO . Formation of persulfate by the action of hydrogen peroxide on sulfites and thiosulfates is also known.

The cumulation of the experimental data of the present investigation enables us to confirm that polythionates are built up from sulfite and thiosulfate groups and that the processes of their formation, reciprocal transformations and decomposition proceed by way of addition, exchange or cleavage of these groups. Other investigations using labeled sulfur lead to the same conclusion [1, 3]. The hypothesis that the reversible reactions



proceed by transfer of sulfur atoms [25] is incorrect.

The data reported fully confirm the chain-like distribution of sulfur atoms in polythionates and their structure, which was advanced by D.I. Mendeleev.

SUMMARY

1. With the help of labeled sulfur the main reactions of formation of trithionate have been studied.
2. In the preparation of trithionate by the action of sulfur dichloride on bisulfite, the first step is formation of sulfoxylic acid, the hydroxyl groups of which are then substituted by sulfite groups.
3. In the preparation of trithionate by the action of sulfur dioxide on thiosulfate, the first step again is formation of sulfoxylic acid, the hydroxyl groups of which are then replaced by thiosulfate groups with formation of pentathionate. In subsequent steps the substitution of thiosulfate groups by sulfite groups gives tetra- and trithionate.
4. In the preparation of trithionate by the action of hydrogen peroxide on thiosulfate, the first product is a symmetrical product of oxidation of the latter — probably dithionate. Replacement of the latter's sulfite group by thiosulfate gives trithionate.
5. Confirmation is obtained of D.I. Mendeleev's proposed structure of polythionates. The reactions of the latter involve addition, cleavage and exchange of entire sulfite and thiosulfate groups.
6. The incorrectness of the theories advanced in some investigations about the modes of formation and transformations of polythionates is demonstrated.

* The experimentally established equilibrium $\text{S}_2\text{O}_6^{--} + \text{S}_2\text{O}_6^{--} = 2\text{S}_4\text{O}_6^{--}$, likewise governing the exchange of thiosulfate groups by sulfite groups, can lead only to a difficultly detectable increase in the activity of the middle sulfur of trithionate from $3/4$ to $13/16$ of the starting activity.

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Received February 15, 1954

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* T. p. = C. B. translation pagination.

INVESTIGATION OF THE LIQUIDUS CURVE IN BINARY SYSTEMS
FORMED BY THE SODIUM SALTS OF FATTY ACIDS
WITH SODIUM NITRATE AND THIOCYANATE

N. M. Sokolov

The properties of sodium salts of fatty acids in melts have not been extensively studied. Thus it comes about that among the large number of binary systems investigated by methods of physicochemical analysis there are no systems comprising salts of fatty acids and sodium nitrate or sodium thiocyanate.

The present research is the first devoted to the examination of this type of system by the method of visual-polythermal analysis. The components of the systems were chosen with a view to comparison of data on the homology and isomerism of salts of fatty acids. To this end we selected salts of formic, acetic, propionic, butyric, caproic, isobutyric and isovaleric acids. With these components it is possible to observe the change of properties of the salts with increasing number of carbon atoms in the radical and with isomerization of the radical.

The fusibility curves of the systems containing nitrate and thiocyanate and an identical fatty acid salt are surprisingly similar. This circumstance prompted us to study the previously uninvestigated system of sodium nitrate - sodium thiocyanate.

The components of the systems - sodium salts of fatty acids [1], sodium nitrate [2] and sodium thiocyanate [3] - melt without decomposition. Certain components can even be heated above their melting points. Thus, formate tolerates heating to 310° [4], acetate to 390° [5], and nitrate to 380° [2], while the thiocyanate does not decompose even when heated to 500° [3].

The literature reports explosion of a mixture of potassium nitrate and sodium acetate on heating [6]; elsewhere the flammability of a heated mixture of sodium thiocyanate and sodium nitrate is reported [7]. We carried out heating of a mixture of salts of fatty acids and sodium nitrate up to 400° and no explosion resulted; mixtures of sodium nitrate and thiocyanate melted quietly and did not inflame at 330-340°. On strong superheating, however, of the melt of a mixture of fatty acid salt and nitrate, gas first began to come off, the temperature rose sharply and, finally, there was an intense flash. This occurs at temperatures at which sodium nitrate decomposes with evolution of gases - oxygen and oxides of nitrogen [8]. It is possible that the cause of the explosions, flashes and inflammations is the reaction of the gaseous products of decomposition of the nitrate with salts of fatty acids and thiocyanates.

Salts of fatty acids with up to four carbon atoms in the radical in admixture both with nitrates and thiocyanates give transparent melts on heating which after solidification satisfactorily withstand repeated remeltings. Systems containing isovalerates and valerates also melted to form transparent liquids, but these had poor stability on remelting and darkened after slight superheating. Systems containing caproate melted to form dark liquids in which the development of the first crystals could be observed with difficulty. These systems readily decomposed when superheated. Additions to these systems of sodium acetate stabilized them and enabled study of the ternary systems of caproate, acetate and sodium nitrate, and caproate, acetate and sodium thiocyanate.

EXPERIMENTAL

The salts were melted in a test tube which was inserted in a broader test tube to ensure more uniform heating. Use was made of a nichrome-constantan thermocouple and a millivoltmeter with mirror reading to 17 mV. The calibration curve was plotted from the following melting points: water 0°, benzoic acid 122°, mannitol 166°, silver nitrate 208°, cadmium 321°, potassium nitrate 337°, and potassium bichromate 398°. On the basis of this calibration curve the melting points of the sodium salts used as components of our systems were: formate 258°, acetate 331°, propionate 298°, butyrate 330°, valerate 357°, caproate 365°, isobutyrate 260°, isovalerate 262°, nitrate 308°, and thiocyanate 311°.

The investigation was carried out with commercial preparations of sodium nitrate and thiocyanate, while the remaining salts were synthesized, starting from the fatty acids and sodium bicarbonate. Commercial sodium nitrate was purified by the method of Laiti • [9]. Sodium thiocyanate (pure for analysis) was twice recrystallized, first from

• Translator's note: Spelling doubtful (unable to trace).

TABLE 1

Systems of sodium salts of fatty acids and sodium nitrate

Sodium nitrate (in mole-%)	Temperature of start of crystallization in systems formed by							Caproate
	Formate	Acetate	Propionate	Butyrate	Isobutyrate	Valerate	Isovalerate	
0	258	331	298	330	260	357	262	365
5	252	328	294	329	248	366	273	376
10	242	324	291	325	242	372	280	383
15	232	318	287	315	238	369	280	385
25	214	304	282	283	219	350	265	375
27	—	—	—	276	—	—	—	—
30	206	296	280	274	233	336	257	367
31.2	—	—	—	—	—	—	254	—
35	198	286	276	273	244	320	260	357
40	192	276	273	271	258	296	272	342
40.5	—	—	—	—	—	295	—	—
45	188	263	269	268	267	294	282	326
49	186	—	—	—	—	—	—	—
50	190	247	264	267	274	295	288	313
55	206	233	258	276	276	288	294	296
56.5	—	—	255	—	—	—	—	287
58	—	224	—	—	—	—	—	—
58.5	—	—	—	—	—	291	—	—
59	—	—	—	—	—	—	—	300
60	220	231	261	283	280	285	299	302
65	235	242	270	288	284	293	302	—
75	262	264	280	296	288	298	304	Layer formation from 60 to 99.84% sodium nitrate
85	284	284	290	298	292	300	306	
95	302	304	301	302	300	305	307	
100	308	308	308	308	308	308	308	

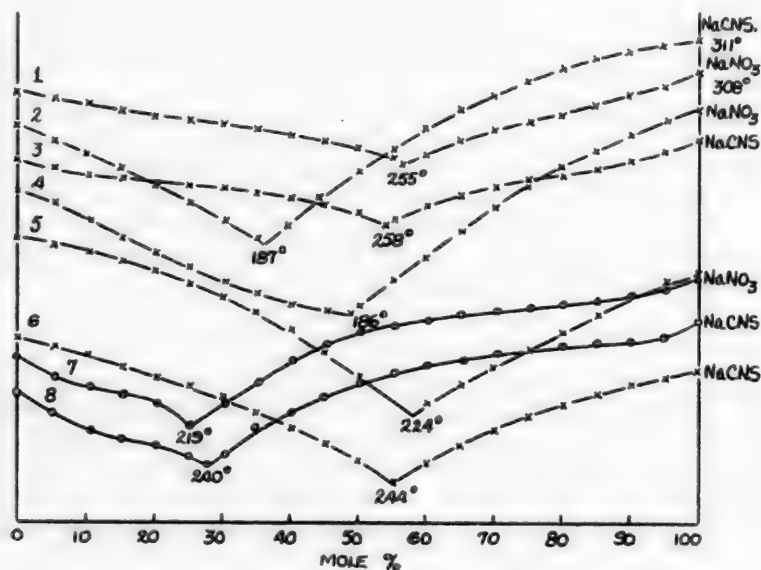


Fig. 1. Liquidus curves of the systems.

Sodium nitrate - sodium propionate (1), - sodium formate (4), - sodium acetate (5), - sodium isobutyrate (7); sodium thiocyanate - sodium formate (2), - sodium propionate (3), - sodium acetate (6), - sodium isobutyrate (8).

TABLE 2

Systems of sodium salts of fatty acids and sodium thiocyanate

Sodium thiocyanate (in mole-%)	Temperature of start of crystallization in systems formed by:							
	Formate	Acetate	Propionate	Butyrate	Isobutyrate	Valerate	Isovalerate	Caproate
0	258	331	298	330	260	357	262	365
5	250	326	292	328	247	370	277	383
10	241	320	289	324	237	378	287	397
15	233	313	287	316	231	375	288	399
25	213	302	282	291	221	356	270	386
27.4	—	—	—	—	214	—	—	—
30	202	295	280	275	221	344	256	377
31.5	—	—	—	268	—	—	—	—
32	—	—	—	—	—	—	250	—
35	190	287	276	266	240	331	260	366
36	187	—	—	—	—	—	—	—
40	197	278	273	264	255	316	272	352
45	212	268	270	263	266	296	285	342
46	—	—	—	—	—	289	—	—
48.5	—	—	—	262	—	—	—	—
50	232	256	265	269	274	291	291	330
54	—	—	258	—	—	—	—	—
54.5	—	244	—	—	—	—	—	—
55	244	245	261	280	280	288	297	316
56.5	—	—	—	—	—	287	—	—
60	256	258	269	287	284	290	300	305
63	—	—	—	—	—	—	—	295
65	267	266	276	290	288	293	303	297
75	284	282	285	298	295	297	305	304
90	302	302	298	304	300	302	306	307
100	311	311	311	311	311	311	311	311

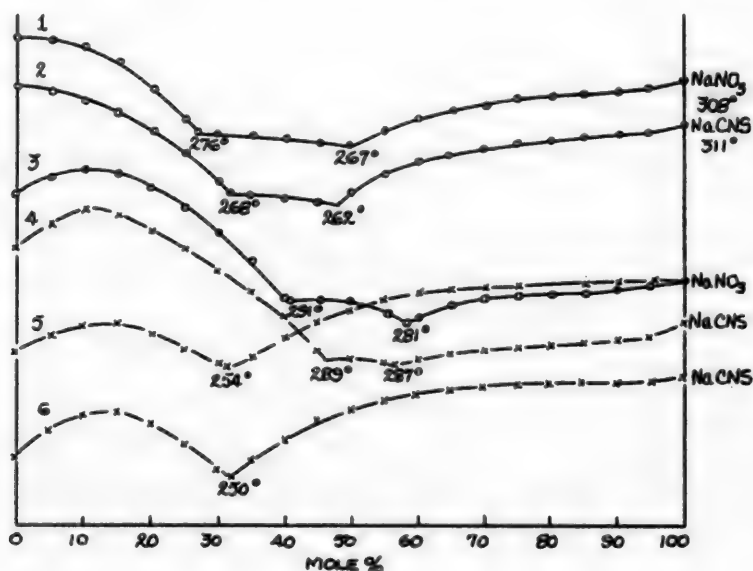


Fig. 2. Liquidus curves of the systems.

Sodium nitrate - sodium butyrate (1), - sodium valerate (3), - sodium isovalerate (5); sodium thiocyanate - sodium butyrate (2), - sodium valerate (4), - sodium isovalerate (6).

TABLE 3

Intersection of branches of liquidus curves

Systems	Temperature	NaNO ₃ (in mole-%)	Temperature	NaCNS (in mole-%)
Formate	186°	49	187°	36
Acetate	224	58	244	54.5
Propionate	255	56.5	258	54
Butyrate { E• P••	267	50	262	48.5
	276	27	268	31.5
Isobutyrate	219	25	240	27.4
Valerate { E ₁ E ₂	291	40.5	289	46
	281	58.5	287	56.5
Isovalerate	254	31	250	32
Caproate	287	56.5	295	63

• E - eutectic point

•• P - transition point

water and then from alcohol; its crystals are very hygroscopic; it is more convenient to melt it before use. The thiocyanate melts at 311°; according to the literature it has m.p. 287° [10] and 326° [11]. We failed to obtain a salt with the higher melting point by synthesizing it from ammonium thiocyanate and caustic alkali or by recrystallization, or by precipitation with ether from a saturated alcoholic solution.

The experimental data are set forth in the tables, and the liquidus curves are plotted in three diagrams.

The liquidus curves of systems formed with sodium salts of fatty acids

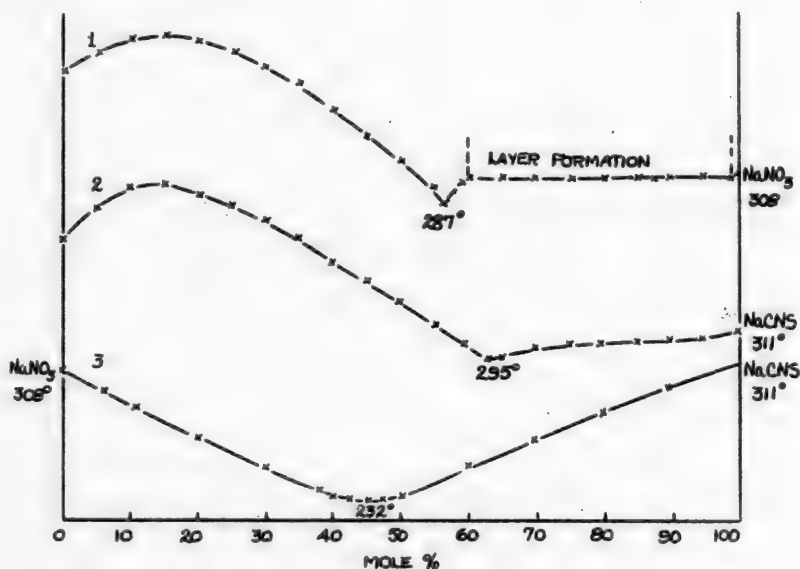


Fig. 3. Liquidus curves of the system

1 - sodium nitrate - sodium caproate, 2 - sodium thiocyanate - sodium caproate,

3 - sodium thiocyanate - sodium nitrate.

TABLE 4

System sodium nitrate - sodium thiocyanate

Thiocyanate (in %)	0	10	20	30	40	45	50	60	70	80	90	100
Temperature of start of crystallization	308	288	268	252	236	232	236	253	269	285	299	311

and sodium nitrate show that in systems containing formate, acetate and propionate there is no complex formation; complex formation is observed in systems containing salts of n-butyric and n-valeric acids. There is no complex formation in systems containing salts of isobutyric and isovaleric acids. Sodium caproate and sodium nitrate have limited mutual solubility in the melted state, and since sodium stearate does not mix at all with sodium nitrate, we can assume that

salts with more carbon atoms in the radical than caproate will be still less miscible with sodium nitrate in the liquid state (Table 3).

Examination of the liquidus curves of systems formed by salts of fatty acids and sodium thiocyanate shows that, just as in the case with systems containing nitrate, complex formation occurs in the butyrate and valerate systems; systems formed from formate, acetate, propionate, caproate, isobutyrate and isovalerate are characterized by eutectic melting (Table 3).

The great similarity between systems containing thiocyanate and nitrate and the same fatty acid salt makes it interesting to investigate the liquidus curve (not previously studied) of the system sodium nitrate - sodium thiocyanate.

The liquidus curve (Fig. 3) has one branch. In the system is formed a continuous series of solid solutions with a minimum at 232° and 45% sodium thiocyanate.

EVALUATION OF RESULTS

Sodium nitrate and thiocyanate have very similar melting points (308 and 311°) and form a continuous series of solid solutions. Comparison of the liquidus curves of systems containing nitrate with the liquidus curves of systems containing thiocyanate show that when the same fatty acid salt is present in these systems they actually exhibit great similarity. On this basis it is suggested that identical processes take place in such systems during crystallization.

On considering the systems in the order of increasing number of carbon atoms in the radicals of the fatty acid salt component, we see that complex formation does not occur when the paraffinic portion of the molecule is of small size. With increasing number of carbon atoms in the radicals of normal structure, ability to form complexes is first developed and then disappears. Thus caproate does not form compounds either with nitrate or thiocyanate, while sodium stearate is not miscible with them at all.

On comparing systems formed by butyrate and valerate with those formed by isobutyrate and isovalerate, we see that salts containing a branched chain of carbon atoms in the radical do not form compounds; they also possess lower melting melting points than salts of normal structure.

The branches of primary crystallization in the case of isovalerate, valerate and caproate are very similar among themselves. In all cases with increasing content of nitrate or thiocyanate the curve at first rises, reaches a certain maximum and then descends. Such a type of curve with a maximum at the branch of one of the components points to the presence of one-sided solid solutions, as had previously been experimentally demonstrated for the systems sodium sulfate - calcium sulfate [12], silver chloride - cadmium chloride [13], and others. It is possible that also in our systems containing isovalerate, valerate and caproate there is formation of one-sided solid solutions.

SUMMARY

1. An investigation was made of the liquidus curves of 17 binary systems, eight of which contain fatty acid salts and sodium nitrate, eight contain the same fatty acid salts and sodium thiocyanate, while one is the system sodium nitrate - sodium thiocyanate.
2. It is shown that the properties of salts of fatty acids in melts change with the number of carbon atoms in the radical and with the isomeric form.

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Received February 9, 1954

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THE SYSTEM ACETIC ANHYDRIDE - NITRIC ACID

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Mixtures of nitric acid and acetic anhydride are used for nitration of organic compounds. The main value of such mixtures is that nitration can be effected usually at low temperatures. The absence under these conditions of processes of oxidation and of nitration to polynitro compounds enables purer products to be obtained, and the yields are higher than when nitrating in presence of sulfuric acid. A second advantage is that when such mixtures are used to nitrate aromatic hydrocarbons which are already substituted, the yield of o-nitro compounds is considerably higher than after nitration in any other medium. In individual cases (nitration of aniline), the amount of o-isomer is nearly 100%. Finally, it is possible with such mixtures to obtain products which cannot be obtained under the usual nitration conditions (nitro derivatives of phenanthrene, anthracene and hydroxycarbazole).

The first steps in the examination of the system acetic anhydride - nitric acid were taken by Pictet [1, 2] who suggested that acetyl nitrate was formed in mixtures of acetic anhydride and nitric acid and diacetylorthonitric acid in mixtures of acetic and nitric acids.

In subsequent investigations of the kinetics of nitration of benzene, it was suggested that nitric acid reacts with the solvent [3].

Renewed interest has been shown in recent years in the system acetic anhydride-nitric acid. On the basis of measurements of the vapor tension the hypothesis was advanced of the formation in the system of acetyl nitrate and nitrogen pentoxide [4]. Chedin and Fénéant [5] confirmed this hypothesis by data for the Raman spectra of mixtures of acetic anhydride and nitric acid. The authors considered the formation of nitrogen pentoxide to be the primary step and that of acetyl nitrate the second step in the process



In a study of the mechanism of nitration of aromatic hydrocarbons, Gold, Hughes and Ingold [6] arrived at the following reversible reactions:



For investigation of the system acetic anhydride-nitric acid we prepared mixtures of acetic anhydride and nitric acid of strictly specific percentage composition.

The nitric acid needed for their preparation was purified by vacuum distillation by Mishchenko's method [7].

We made a slight modification when assembling the distillation apparatus. The nitric acid which did not condense was absorbed by water in 2 to 3 wash bottles. In front of the first wash bottle (bubbler for nitric acid) was arranged a sulfuric acid wash bottle to protect the nitric acid against access of moisture when air was blown into the system. Distillation was carried out with a water jet pump. Acid containing 99.80-99.9% nitric acid was used. The concentration of the nitric acid was determined by titration with 0.5N alkali solution in presence of phenolphthalein. The absence of lower oxides of nitrogen in the nitric acid was checked with potassium permanganate.

The acetic anhydride and acetic acid were purified by repeated distillation of the technical product in a column. The fraction of acetic anhydride selected had b.p. 139-140° at 760 mm, and the acetic acid fraction had b.p. 117.4-117.8° at 753 mm.

After preparation, the solutions of nitric acid and acetic anhydride were kept in ice in the course of several hours' working with them.

The atomic concentration* of the system [8-10] and the magnitude of ΔA , which represents the difference between the optimum values of the atomic concentration and its additive values, were calculated for the temperature of 0°. The density of the individual mixtures required for the calculation was determined in a pycnometer with a capillary or in a pycnometer with a graduated scale. Determinations were carried out in a

* Translator's note. The atomic concentration is the total number of gram-atoms per liter.

thermostat. The temperature was maintained between 0.05 and 0.15°.

Density (without corrections) was obtained from the weight in air. Correction for the weight had no effect at all on the magnitudes of ΔA and Δd which were of interest to us in this research.

The experimental values of the density of solutions of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$ (d), the deviations of atomic concentration from the additive values (ΔA), and the magnitudes required for their calculation — the experimental atomic concentration (A) and the additive density (d_u) — are set forth in Table 1.

TABLE 1
Density and atomic concentration of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$ at 0°.

Composition of mixture (in volume-%)		d, g/ml	d_u , g/ml	Δd , g/ml	A_u	ΔA
HNO_3	$(\text{CH}_3\text{CO})_2\text{O}$					
0.00	100.00	1.1011	1.1011	0.0000	140.2	0.0
5.62	94.38	1.1167	1.1262	-0.0095	139.2	-1.2
7.55	92.45	1.1245	1.1347	-0.0102	138.9	-1.3
10.12	89.88	1.1327	1.1462	-0.0135	138.4	-1.6
14.97	85.03	1.1484	1.1678	-0.0194	137.6	-2.3
22.84	77.16	1.1751	1.2029	-0.0287	136.2	-3.2
30.11	69.89	1.2025	1.2352	-0.0327	135.0	-3.6
35.01	64.99	1.2231	1.2570	-0.0339	134.1	-3.6
40.00	60.00	1.2473	1.2792	-0.0319	133.2	-3.3
45.82	54.18	1.2763	1.3052	-0.0289	132.2	-2.9
52.04	47.96	1.3072	1.3329	-0.0257	131.1	-2.5
58.96	41.04	1.3453	1.3637	-0.0184	129.9	-1.8
66.85	33.15	1.3943	1.3988	-0.0045	128.5	-0.4
74.68	25.32	1.4515	1.4337	0.0178	127.1	1.6
79.89	20.11	1.4881	1.4569	0.0312	126.2	2.6
82.60	17.40	1.5028	1.4690	0.0322	125.8	2.8
85.04	14.96	1.5122	1.4799	0.0323	125.3	2.7
90.08	9.92	1.5200	1.5023	0.0177	124.5	1.5
100.00	0.00	1.5465	1.5465	0.0000	122.7	0.0

The dependence of ΔA on the composition of the system is plotted in Fig. 1; in the same diagram is plotted the isotherm of Δd . The shape of the isotherm of ΔA , obtained by us for the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$, is a fairly common form of the composition — property curve with a maximum and a minimum. The position of the minimum corresponds almost exactly to the composition of a mixture of 1 mole acetic anhydride and 1 mole nitric acid; hence it is difficult to account for the formation of a minimum solely on the basis of dissociation of the associated component. Moreover, in the literature we failed to find any indication of the association of acetic anhydride molecules. We suggest that the minimum of the ΔA isotherm is due to formation of acetyl nitrate in the system



Since the number of molecules in the system remains unchanged in formation of acetyl nitrate, the spread must be attributed to the less electrovalent character of the products on the right-hand side of the equation.

The maximum, which corresponds to the molar ratio of nitric acid to acetic anhydride, is equal to 11:1, and it adequately reflects the sharp structural change in the system since only one mole of acetic anhydride per 11 moles acid results in the very high value of $\Delta A = 2.8$ g-at/l. Above all we consider it necessary to draw attention to the fact that acetic acid, which is formed when acetyl nitrate is formed in the system and which is reported in the literature to react with nitric acid, cannot in this range of concentrations give such a large deviation of atomic concentration.

The system acetic acid—nitric acid has been studied in detail by Miskidzhyan and Trifonov [11-13], as well as by Naumova [14]. However, these authors were not directly concerned with the study of the density of the system acetic acid—nitric acid at 0°; hence the accuracy of the density values taken from their papers could not satisfy us.

Results of investigations of the system $\text{CH}_3\text{COOH}-\text{HNO}_3$ are set forth in Table 2 and plotted in Fig. 2.

If we now regard the positive values of ΔA in the system acetic anhydride—nitric acid as the consequence of formation of acetic acid, then we must assume that our isotherm of ΔA (Fig. 1) is the sum of two curves, the first of which reflects the formation of acetyl nitrate and moves downwards from the abscissas, while the second reflects the result of interaction of acetic acid with nitric acid and moves upwards from the abscissas. The observed maximum is in this sense only cut off by the end of the upper curve. It should follow from this, however, that the maximum value of ΔA of the system acetic acid—nitric acid at 0° must be very high. Actually, we did

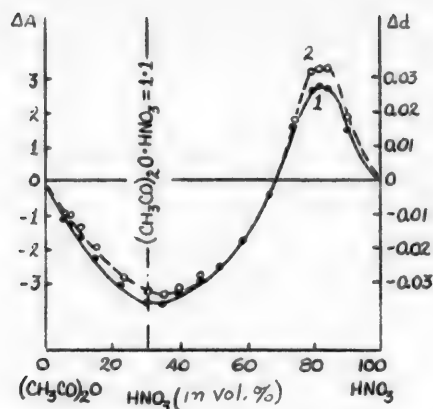


Fig. 1. ΔA (1) and Δd (2) of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$ at 0° .

TABLE 2

Specific gravity and atomic concentration of the system $\text{CH}_3\text{COOH}-\text{HNO}_3$ at 0°

Composition of mixture (in volume-%)		$d, \text{g/ml}$	$d_u, \text{g/ml}$	$\Delta d, \text{g/ml}$	A_u	ΔA
HNO_3	CH_3COOH					
0.00	100.00	1.0708	1.0708	0.0000	142.65	0.0
10.11	89.89	1.1260	1.1189	0.0071	140.6	0.9
10.13	89.87	1.1270	1.1190	0.0080	140.6	1.0
20.08	79.92	1.1808	1.1664	0.0144	138.7	1.7
29.91	70.09	1.2320	1.2132	0.0188	136.7	2.1
39.83	60.17	1.2822	1.2604	0.0218	134.7	2.3
44.76	55.24	1.3065	1.2838	0.0227	133.7	2.4
47.82	52.18	1.3213	1.2984	0.0229	133.1	2.4
50.85	49.15	1.3358	1.3128	0.0230	132.5	2.3
53.90	46.10	1.3499	1.3273	0.0226	131.9	2.3
57.04	42.96	1.3642	1.3423	0.0219	131.3	2.1
59.60	40.40	1.3758	1.3545	0.0213	130.8	2.1
62.98	37.02	1.3905	1.3706	0.0199	130.1	1.9
66.02	33.98	1.4042	1.3850	0.0192	129.5	1.8
69.99	30.01	1.4211	1.4039	0.0172	128.7	1.6
74.90	25.10	1.4419	1.4273	0.0146	127.7	1.3
80.15	19.85	1.4624	1.4523	0.0101	126.7	0.9
100.00	0.00	1.5468	1.5468	0.0000	122.7	0.0

and below we advance considerations about the possible mechanism of its formation.

In comparing the isotherms of ΔA and Δd of the system acetic anhydride-nitric acid (Fig. 1), we must mention that the maximum of both curves corresponds substantially to one and the same composition of the system - 82-83 vol.-% HNO_3 . The minimum of the isotherms in both cases also corresponds to an identical concentration of nitric acid (35 vol.-%). This is clear evidence that both of the processes taking place in the system are not complicated by side reactions of the products formed with the starting components of the mixture, and it may serve as confirmation of the fact that acetyl nitrate is by no means an intermediate compound in the process of formation of nitrogen pentoxide.

The viscosity of mixtures of the system acetic anhydride-nitric acid was measured in an Oswald viscometer of the usual type. During the period of keeping of the viscometer in the thermostat with mixtures of one or the other component of the mixture, a rubber tube with screw clips was placed over it to protect the contents against access of moisture.

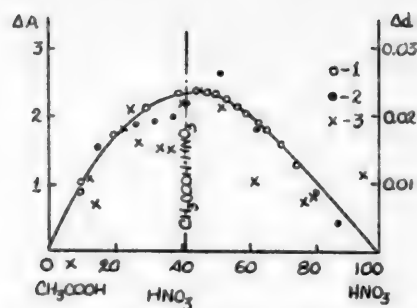


Fig. 2. ΔA and Δd of the system $\text{CH}_3\text{COOH}-\text{HNO}_3$ at 0° . 1) ΔA from the data of our measurements; 2) ΔA from data of Miskidzhyan and Trifonov; 3) Δd from data of Naumova.

not observe this (Figs. 1 and 2). The ordinate of the maximum of the isotherm of ΔA in the system acetic anhydride-nitric acid is 2.8 g-at/l, and the position of the maximum corresponds to the ratio of acetic acid separated on formation of acetyl nitrate to the acetic acid not bound as acetyl nitrate. This ratio is 1:1.0, but the ordinate of ΔA in the system acetic acid-nitric acid in the corresponding field of concentrations is only 0.6 g-at/l. Consequently, the maximum of the isotherm of ΔA in the system acetic anhydride-nitric acid cannot be accounted for by interaction with nitric acid of the acetic acid formed in the system.

We are of the opinion that in this part of the system nitrogen pentoxide is formed,

Determinations were carried out at 0° and 10°. Determinations at 10° were carried out in the course of 20-25 minutes. Prior to these measurements the mixtures were kept, as usual, at a temperature not higher than 0°, so that during the period of determination no far-reaching decomposition of the system was observed.

The relative viscosity of the system acetic anhydride-nitric acid (in millipoises) in dependence on the molecular composition is set forth in Table 3 and plotted in Fig. 3.

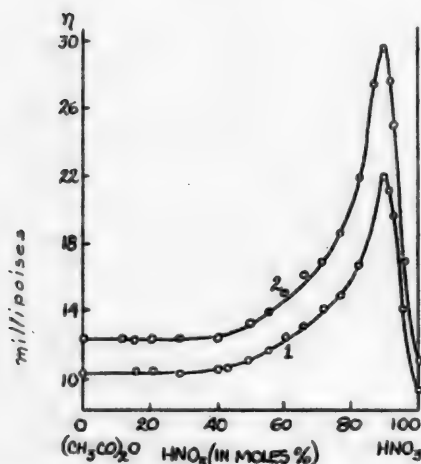


Fig. 3. Viscosity of the system acetic anhydride-nitric acid $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$. 1) 10°, 2) 0°.

The viscosity isotherms contain small but well-marked maxima in the right-hand portion of the diagram. The position of the maxima in relation to the abscissas corresponds to 90 mole-% nitric acid, i.e., approximately the same composition of system as for the maximum of atomic concentration. On raising the temperature to 10° the absolute magnitude of the maximum falls slightly, but its position in relation to the abscissas remains unchanged. On the left hand part of the diagram the isotherms have a direction parallel to the abscissas with an inflection in the curve in the range of 40-50 mole-% HNO_3 .

In our opinion the maximum of the isotherms marks the formation in the system of the maximum amount of nitrogen pentoxide. The formation of acetyl nitrate, however, is not accompanied by considerable changes of the viscosity of the system.

The refractive index of the system acetic anhydride-nitric acid was measured in an Abbe refractometer (a saccharimeter with stationary prisms). Measurements were performed at 0-0.5°. Owing to inability to reduce the temperature variations to a lesser degree, the accuracy of our determinations does not exceed $5 \cdot 10^{-4}$.

In Table 4 are set forth the refractive indices in dependence on composition. In Fig. 4 is plotted the isotherm of the refractive index (curve 1). The curve of deviation from additivity (curve 2) exhibits more definitely a minimum in respect to the abscissas at 50 mole-% HNO_3 and a maximum at a concentration of 91 mole-%.

For explanation of the suggested processes we think the most probable assumption is that the molecule of acetic anhydride behaves like a base in presence of nitric acid, adding on a proton to form an acetic anhydride cation $-(\text{CH}_3\text{CO})_2\text{OH}^+$. This cation then dissociates into acetic acid and acetyl ion. The latter reacts with nitrate ion to form another molecule of acetyl nitrate:

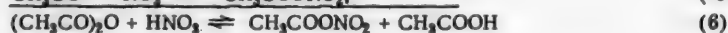


TABLE 3

Viscosity of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$ at 0° and 10°

Composition of mixture (in mole-%)		η^0 (millipoises)	η^{10} (millipoises)
HNO_3	$(\text{CH}_3\text{CO})_2\text{O}$		
0.00	100.00	12.28	10.32
11.94	88.06	12.30	—
15.68	84.32	12.29	10.38
20.39	79.61	12.34	10.40
28.60	71.40	12.27	10.35
40.25	59.75	12.40	10.43
42.98	57.02	—	10.64
45.36	54.64	12.76	—
49.51	50.49	13.09	11.03
55.07	44.93	13.98	11.63
60.27	39.73	15.03	12.45
65.81	34.19	16.04	13.13
71.17	28.83	16.92	14.07
76.57	23.43	—	14.92
76.69	23.31	18.51	—
82.11	17.89	21.84	16.72
87.03	12.97	27.50	20.31
90.04	9.96	29.63	21.96
91.53	8.47	27.86	21.20
92.82	7.18	25.11	19.66
92.38	4.62	16.97	14.08
100.00	0.00	10.99	9.35

TABLE 4
Refractive index of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$

Composition of mixture (in mole-%)		n_D°	Composition of mixture (in mole-%)		n_D°
HNO_3	$(\text{CH}_3\text{CO})_2\text{O}$		HNO_3	$(\text{CH}_3\text{CO})_2\text{O}$	
0.00	100.00	1.3993	66.79	33.21	1.3975
11.29	88.71	1.3975	73.88	26.12	1.4010
20.16	79.84	1.3965	77.13	22.87	1.4025
27.87	72.13	1.3959	84.35	15.65	1.4077
35.69	64.31	1.3949	87.85	12.15	1.4117
43.77	56.23	1.3935	90.18	9.82	1.4145
49.36	50.64	1.3936	92.94	7.06	1.4122
55.48	44.52	1.3942	95.40	4.60	1.4082
59.95	40.05	1.3960	100.00	0.00	1.4055

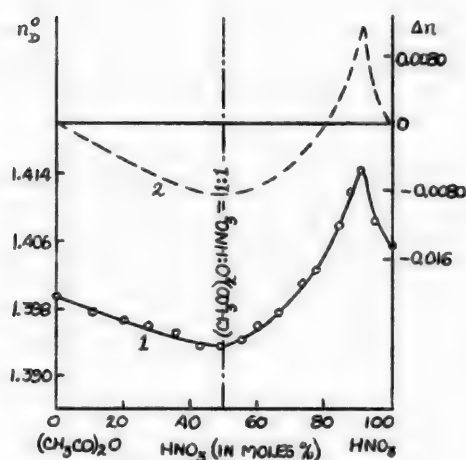


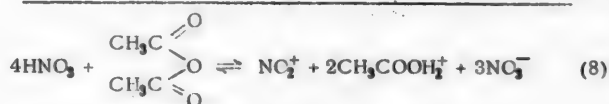
Fig. 4 Refractive index of the system $(\text{CH}_3\text{CO})_2\text{O}-\text{HNO}_3$.
1) n_D° , 2) Δn .

Even an insignificant amount of acetyl cation in the system proves sufficient for formation of acetyl nitrate.

On the basis of the ΔA diagram we must conclude that the process of formation of acetyl nitrate proceeds substantially completely from left to right at equimolecular concentration of components and becomes extremely insignificant at a nitric acid concentration of 80-90 mole-%.

In the region of predominating concentrations of nitric acid we suggest that nitrogen pentoxide is formed.

We consider the formation of nitrogen pentoxide in the system to be possible in accordance with the following scheme:



According to current ideas about the dissociation of nitric acid and its aqueous solutions, close to 100% equilibrium (7a) also exists in nitric acid as such. On adding acetic anhydride to nitric acid, the former reacts with the hydroxonium ion to form a molecule of acetic acid and a cation of acetic acid (7b). The formed molecule of acetic acid removes from the system the subsequent molecule of nitric acid (7c). The over-all equation of the proposed reactions is represented by equation (8). Equilibria (9) and (10) are possible for the products of the right-hand side of this equation. Equation (9) represents the process of formation of nitrogen pentoxide in the system. The process of formation of the undissociated form of nitrogen pentoxide and the process expressed by equation (7b) shift the reaction of dissociation of nitric acid to the right. With excess of nitric acid, the disturbed state will be restored by dissociation of the subsequent molecules of nitric acid of the acid-base type.

From the ΔA diagram it follows that the maximum shift of the process expressed by equation (7a) to the right (maximum concentration of nitrogen pentoxide) occurs at a concentration of 91 mole-% nitric acid. On the viscosity diagram the process of formation of nitrogen pentoxide is characterized by a maximum in the region of 90 mole-%; on the refractive index diagram it is marked by a maximum for the mixture containing 91 mole-% nitric acid.

Consequently, contrary to the view of Chedin and Fénéant, on the one hand, and to the view of Gold, Hughes and Ingold on the other hand, we suggest that, in dependence on the ratio of concentrations of starting components, either the reversible process of reaction of acetic anhydride with nitric acid, with formation of acetyl nitrate, or the process of formation of nitrogen pentoxide due to reaction of nitric acid with acetic anhydride will prevail in the system.

To summarize our observations on the system acetic anhydride-nitric acid, we may say that the atomic concentration and refractive index point both to the formation of acetyl nitrate in the system and to formation of nitrogen pentoxide. The viscosity of the system clearly reflects only the process resulting in formation of nitrogen pentoxide.

SUMMARY

1. Determinations were made of the density at 0°, viscosity at 0° and 10° and refractive index at 0° in the system acetic anhydride-nitric acid.
2. Deviations of the atomic concentration from additivity— ΔA —reveal the occurrence in the system of two equilibrium processes of interaction of acetic anhydride with nitric acid: formation of acetyl nitrate in the region of equimolecular concentrations and formation of nitrogen pentoxide in the region of very high concentrations of nitric acid. In the first stage of both processes, acetic anhydride functions as a base.
3. The isotherm of deviation of the refractive index from additivity likewise reflects the above-mentioned processes.
4. The viscosity of the system clearly reflects only the process of formation of nitrogen pentoxide.
5. The density of the system acetic acid-nitric acid was determined at 0°. From a comparison of the isotherm of ΔA in the system acetic anhydride-nitric acid with the isotherm in the system acetic acid-nitric acid, it follows that such considerable positive deviations of the atomic concentration from additivity in the system acetic anhydride-nitric acid cannot be caused solely by interaction between nitric and acetic acids.

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Received July 1, 1953

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- * See Consultants Bureau English translation page 413.
- ** See Consultants Bureau English translation page 393
- *** See Consultant Bureau English translation page 397
- **** See Consultants Bureau English translation page 1223.

THE REACTION OF ACETONE WITH ANHYDROUS POTASSIUM HYDROXIDE

B. T. Zubakhin

The following reactions between two or three molecules of acetone are known:

- 1) Condensation under the influence of acids with formation of mesityl oxide, phorone and mesitylene.
- 2) Condensation under the influence of aqueous solutions of caustic alkalis with formation of diacetone alcohol.

The problem of the mechanism of "resinification" of acetone under the action of anhydrous caustic alkalis in presence of atmospheric oxygen and the formation of an oily product in the absence of air has remained completely unclarified.

In the present investigation we have succeeded in establishing that on reaction of acetone and other ketones (in particular diethyl ketone) with anhydrous granulated potassium hydroxide, formation takes place of an oily product, the main mass of which distills at 150-360° (see table). The product has a pleasant minty-softwood odor. From the acidic products were separated acetic and pyroracemic acid (in the form of their potassium salts).

The oily product was subjected to fractional distillation. In the table are set forth the temperature ranges of the isolated fractions and for some of them the specific gravities and refractive indices.

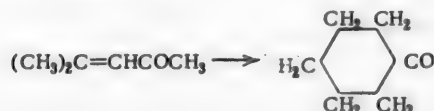
The fractions reacted with semicarbazide acetate, forming semicarbazones which, after many recrystallizations from alcohol, possessed definite melting points, corresponding to the semicarbazones of mesityl oxide, cyclohexanol, d-pulegone, α -thujone, n-isopulegone. On the basis of the yield of semicarbazones it could be concluded that the investigated fractions contained 60-70% keto compounds. After oxidative treatment, the yield of semicarbazones rose to 90-95%, which indicated the presence of 25-35% compounds containing hydroxyl.

The high-boiling fractions were only examined qualitatively.

Fraction number	Boiling range	Weight of fraction (in weight-% of starting product)	d_{15}^{20}	n_D^{21}	Main components of fraction
1	130-170°	—	—	—	—
2	170-190	—	—	—	Cyclohexanone
3	190-220	20	0.910	1.494 ± 1	Isopulegol, isopulegone, thujone and thujyl alcohol
4	220-250	16	—	—	Pulegone
5	250-290	32	0.970	1.527	—
6	290-310	8	—	—	—
7	310-360	14	0.990	1.525	—
	Resinous residue	8-10	1.05	—	—

The boiling points of the various fractions set forth in the table, their specific gravity and refractive index, and the preparation from these fractions of semicarbazones with definite melting points demonstrate that in the action of potassium hydroxide on acetone the products were ketones and alcohols identical with products of the terpene series — mesityl oxide, cyclohexanone, n-isopulegone, α -thujone and, apparently, isopulegol and thujyl alcohol.

These data enable us to advance the following reaction mechanism: At the start two molecules of acetone condense with formation of mesityl oxide. Formation of cyclohexanone may be represented as the consequence of far-reaching rearrangement of mesityl oxide:



Formation of terpene alcohols may be regarded as proceeding according to the following over-all equation:



Ketones of the terpene series are formed by oxidation of terpene alcohols. When the reaction is carried out in absence of air, it evidently stops short at the step of formation of terpene alcohols.

When carrying out the reaction in presence of oxygen of the air, high-boiling products are also formed; on the basis of a series of qualitative tests and of the data set forth in the table, these are sesquiterpenes and diterpenes; at the same time alcohol-soluble and bituminous resins are formed.

EXPERIMENTAL

1. Reaction of acetone with potassium hydroxide. A mixture of 180 ml acetone and 70 g KOH was stood for 7 days at room temperature. The liquid was then decanted from the solid, neutralized, and fractionated to give the fractions shown in the table.

The 1st and 2nd fractions were again subjected to fractional distillation. From the resultant two main fractions could be isolated semicarbazones with m.p. 156 and 166°, which pointed to the presence in the mixture of mesityl oxide and cyclohexanone [1]. From the 3rd and 4th fractions, after fractional distillation and distillation with steam, could be separated several products: a first with b.p. 200-210°, a second with b.p. 210-220°, and a third with b.p. 220-225°.

From the first product was obtained a semicarbazone with m.p. 186°, corresponding to α -thujone [2]. The oily portion of the products which did not react with semicarbazide gave the same semicarbazone after oxidation with chromic acid.

From the third product was obtained a semicarbazone with m.p. 167-168°, corresponding to d-pulegone.

The portions of the 4th fraction non-volatile with steam gave still another semicarbazone with m.p. 182-183°, corresponding to n-isopulegone [3].

Broadly, the same compounds were obtained by boiling acetone in presence of KOH.

Reaction of acetone with KOH on heating in absence of air gave a mobile, oily liquid. No resins or high-boiling derivatives were formed in this reaction. About 5% of semicarbazones were formed.

After oxidative treatment, the part volatile in steam gave two semicarbazones with m.p. 186 and 174°, corresponding to α - and β -thujone.

From the non-volatile portion was obtained isopulegone semicarbazone (m.p. 182-183°).

Consequently, the mixture evidently consisted mainly of thujyl alcohol and isopulegol. In the lower aqueous layer was found about 9% potassium acetate.

When diethyl ketone is stood for a long period with solid, finely granulated potassium hydroxide, a liquid is formed with a pleasant, minty odor. After isomerization in 40% KOH solution, this liquid forms a semicarbazone with m.p. 184°.

SUMMARY

1. It is shown that reaction of acetone with anhydrous KOH in presence of oxygen of the air evidently leads to formation of terpenic alcohols and ketones.
2. Only terpene alcohols appear to be formed when acetone reacts with anhydrous KOH in the absence of air.

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Received June 6, 1952,

February 25, 1954

CATALYTIC PREPARATION OF MIXED KETONES FROM PRIMARY ALCOHOLS

II. KETONIZATION OF A MIXTURE OF ETHYL AND ISOAMYL ALCOHOLS

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In the preceding communication [1] consideration was given to the process of ketonization of a mixture of two primary alcohols of normal structure. It appeared to us of interest to investigate further the characteristics of the ketonization of a mixture of alcohols of normal and iso structure, for example ethyl and isoamyl alcohols. As the results of this work show, on passing such a mixture over the copper-activated catalyst of Dolgov and Bolotov [2] methylisobutyl ketone is obtained in good yield, as well as acetone and diisobutyl ketone in minor amounts.

Optimum conditions for formation of the mixed ketone were established by a study of the influence of temperature, ratio of alcohols in the mixture, space velocity and supplementarily introduced hydrogen.

It follows from experiments with a passage of 1 : 1 (molar ratio) mixture of ethyl and isoamyl alcohols over the catalyst at various temperatures (between 275 and 425°) and constant space velocity (150) that the optimum reaction temperature is 350° (Table 1).

TABLE 1

Experimental temperature	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl isobutyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
Molar ratio 1 : 1							
275°	0.0	1.0	0.4	12.0	30.4	10.1	23.0
300	3.0	6.2	0.6	5.6	30.9	4.4	20.1
325	2.7	12.0	1.8	3.6	16.4	6.4	11.8
350	2.2	18.5	4.1	4.6	9.0	1.8	7.2
375	0.0	10.7	4.9	11.0	8.4	2.8	4.8
400	0.0	10.7	4.0	14.7	2.8	3.9	7.8
425	0.0	8.6	3.6	10.0	0.7	2.0	18.9
Molar ratio 1 : 2							
275	0.0	4.1	0.5	13.2	44.7	9.5	26.0
300	0.0	10.1	1.0	12.6	41.7	4.0	25.1
325	0.0	16.0	0.8	3.8	34.7	2.6	12.6
350	0.0	12.0	6.2	7.2	33.8	3.9	9.0
375	0.0	11.7	10.0	8.9	26.4	9.0	5.6
400	0.0	6.0	2.8	16.7	8.7	5.9	10.9
425	0.0	6.5	1.0	11.1	17.5	5.0	13.8
450	0.0	6.3	5.4	7.8	17.2	5.0	21.6
Molar ratio 2 : 1							
275	2.6	2.3	0.6	9.0	21.0	14.4	9.0
300	0.0	5.0	4.2	5.6	16.3	4.5	3.9
325	0.0	13.3	2.1	4.8	9.0	3.0	3.6
350	1.0	21.0	4.7	0.7	4.0	5.0	1.8
375	0.0	2.8	4.5	4.5	5.0	13.5	4.9
400	0.0	2.6	6.3	1.3	6.4	11.5	8.8

TABLE 2

Space velocity	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl iso-butyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
51	0.8	16.4	6.2	0.5	2.1	3.0	3.4
99	0.6	18.0	5.1	0.5	3.0	4.5	2.5
151	1.0	21.0	4.7	0.7	4.0	5.0	1.8
200	2.0	7.0	4.7	16.7	7.0	12.0	8.0
301	3.5	2.6	4.0	7.7	9.4	25.6	8.2

TABLE 3

Experimental conditions	Yields (in % of starting mixture of alcohols)						
	Acetone	Methyl iso-butyl ketone	Diisobutyl ketone	Isovaleraldehyde	Esters	Ethyl alcohol	Isoamyl alcohol
In presence of hydrogen	1.0	21.0	4.7	0.7	4.0	5.0	1.8
Without hydrogen							
1st hour	0.0	3.9	2.7	17.4	4.5	12.2	9.4
2nd hour	0.0	3.2	2.1	20.9	5.5	16.9	12.6

The slightly higher optimum temperature in this case in comparison with the temperature of the reaction of formation of methyl propyl ketone (325°) [1] is due to the effect of the branching of one of the starting alcohols.

As we see from Table 1, the best ratio of ethyl and isoamyl alcohols from the standpoint of yield of methyl isobutyl ketone is a molar ratio of 2 : 1, at which the mixed ketone is obtained as the main reaction product. Just as in the case of a mixture of ethyl and butyl alcohols, rise of temperature is accompanied by a drop in the yield of esters which at low temperatures reaches 20-45% of the mixed alcohols passed through. The maximum for methyl isobutyl ketone at 350° corresponds to a minimum for isovaleraldehyde. Consequently fresh confirmation is obtained of intermediate formation of aldehydes and esters during ketonization of mixtures of alcohols.

The effect of space velocity on the yields of methyl isobutyl ketone was determined from experiments with a mixture of ethyl alcohol and isoamyl alcohol in the molar ratio of 2 : 1 at 350°, i.e. under the optimum conditions for formation of methyl isobutyl ketone. It follows from inspection of the data of Table 2 that the best yields of mixed ketone are obtained at space velocities of 50-150, further rise of space velocity to 200 sharply reducing the yields. Isovaleraldehyde is obtained in insignificant yield in the region of maximum yields of methyl isobutyl ketone, but its amount rises sharply at a space velocity of 200.

For clarification of the role of hydrogen, a 2 : 1 (molar) mixture was passed over the catalyst at optimum conditions, i.e. at 350° and space velocity of 150°, but in the absence of hydrogen. The experiment was continued for two hours, and the liquid and gaseous products collected after the first and second hour were examined separately. We see from Table 3 that in the absence of hydrogen there is a sharp drop in the yield of methyl isobutyl ketone, accompanied by an equally sharp rise in yield of isovaleraldehyde and a slight rise in the amount of esters.

Performance of the reaction without hydrogen inhibits the steps of condensation of aldehydes to esters and ketones.

EXPERIMENTAL

The ethyl alcohol used in the work was commercial rectified spirit (95%), d^{18}_4 0.805. The commercial isoamyl alcohol was dried over Na_2SO_4 and distilled: b.p. 130.5-132.0°; d^{18}_4 0.816 n^{18}_D 1.4080. The experiments were performed in the apparatus used for ketonization of a mixture of ethyl and butyl alcohols [1]. The liquid condensates from each experiment were fractionated in a rectifying column. The following fractions were usually obtained: 1st 54-60°; 2nd 60-80°; 3rd 80-90°; 4th 90-95°; 5th 95-118°; 6th 113-118°; 7th 118-145°; 8th 145-163°; 9th 163-168°; 10th 168-188°; residue (above 188°). Fractions with identical boiling points from all the fractionations were, after analysis, combined and refractionated in a column in order to isolate the individual substances and to identify them.

The first fraction contained acetone and formed not more than 1-2% of the weight of condensates; it was analyzed for its ketone content by the hydroxylamine method.

The 2nd fraction contained ethyl acetate and isovaleraldehyde. C_2H_6O was determined by difference.

The 3rd and 4th fractions contained isovaleraldehyde, which was determined by the ammoniacal silver method, and water.

The 5th fraction consisted of isovaleraldehyde, methyl isobutyl ketone and water. On refractionation, a fraction corresponding to isovaleraldehyde was separated.

b.p. 91.5-92.5°, n_D^{20} 1.3920.

Literature data: b.p. 92.5°, n_D^{20} 1.39225.

The 2,4-dinitrophenylhydrazone melted at 122.5-123.0 (the literature reports 123.0°).

Found %: N 21.12. $C_{11}H_{14}O_4N_4$. Calculated %: N 21.05.

The 6th fraction contained methyl isobutyl ketone which was isolated and identified after refractionation:

B.p. 115.5-116.5°, d_4^{20} 0.8056, n_D^{20} 1.3973.

Found: M 100.3, 98.8. $C_6H_{12}O$. Calculated: M 100.

The recrystallized semicarbazone had m.p. 130.5-131.0° (literature 132.0°).

Found %: N 27.0. $C_7H_{12}ON_3$. Calculated %: N 26.75.

From the 7th fraction on refractionation was separated 129.5-131.0 and 131-143° fractions.

The 129.5-131.0° fraction was isoamyl alcohol.

The 131-145° fraction contained ethyl isovalerate (b.p. 134.7°) and isoamyl acetate (b.p. 142°). Their presence was confirmed by saponification of the fraction with 25% KOH when 2 fractions of organic acids a and b were obtained; from the latter were prepared the silver salts.

Fraction a. Found %: Ag 51.20. C_4H_9COOAg . Calculated %: Ag 51.65.

Fraction b. Found %: Ag 65.23. CH_3COOAg . Calculated %: Ag 64.65.

The 8th fraction was an intermediate one, very small in quantity and containing diisobutyl ketone (identified by analysis).

The 9th fraction contained diisobutyl ketone which was isolated by refractionation and was identified:

B.p. 165-166°, d_4^{20} 0.8274, n_D^{20} 1.4138.

Literature data: b.p. 168°, d_4^{20} 0.8279, n_D^{20} 1.4120.

The recrystallized semicarbazone had m.p. 121-122° (literature: 121-122°).

Found %: N 21.62. $C_{10}H_{21}ON_3$. Calculated %: N 21.11.

The 2,4-dinitrophenylhydrazone melted at 66.0-66.5° (literature: 66°).

The 10th fraction and the residue contained (by analysis) ketones and esters. Refractionation gave fractions corresponding to isoamyl isovalerate:

B.p. 188-190°, d_4^{20} 0.8577, n_D^{20} 1.4136.

Literature data: b.p. 190.4°, $d_4^{18.7}$ 0.8583, $n_D^{18.7}$ 1.41300.

Found: M 168.3, 168.9. $C_{10}H_{20}O_2$. Calculated: M 172.

The composition of the gas from experiments under conditions most favorable for formation of mixed ketone is characterized by a very high content of hydrogen (about 85%); it also contains CO_2 (5-6%) and CO (5-8%). The olefins content of the gas is very small (2-2.5%), saturated hydrocarbons are absent.

SUMMARY

1. In the formation of methyl isobutyl ketone as the main product of reaction over activated copper catalyst, the optimum conditions are a molar ratio of ethyl and isoamyl alcohols in the starting mixture of 2:1, a temperature of 350°, and a space velocity of 50-150. Under these conditions the yield of methyl isobutyl ketone is 18-21% on the starting mixture, that of acetone is 0.6-1%, and that of diisobutyl ketone about 5%. The overall yield of ketones is not less than 24-26% reckoned on the starting mixture.

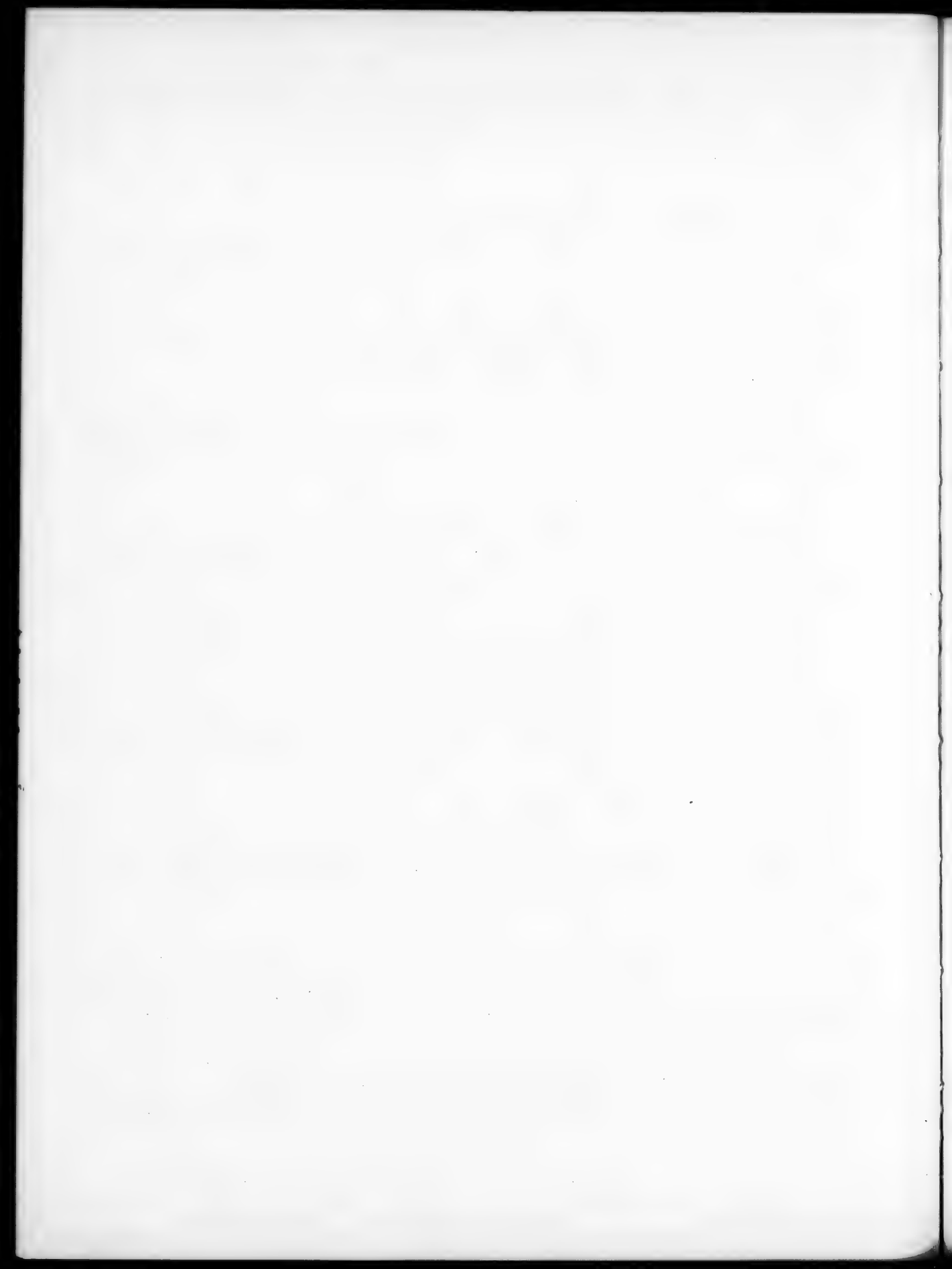
2. At low experimental temperatures (275-300°) high yields of esters (up to 45%) are obtained. Among the reaction products are ethyl acetate, isoamyl acetate, ethyl isovalerate and isoamyl isovalerate.

3. The slightly higher optimum temperature for formation of methyl isobutyl ketone in comparison with that for methyl propyl ketone is explained by the effect of the branched structure of one of the starting components.

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Received December 26, 1953. Leningrad State University



CATALYTIC SYNTHESIS OF KETONES

III. SYNTHESIS OF METHYL ETHYL, METHYL-n-BUTYL AND METHYLISOBUTYL KETONES

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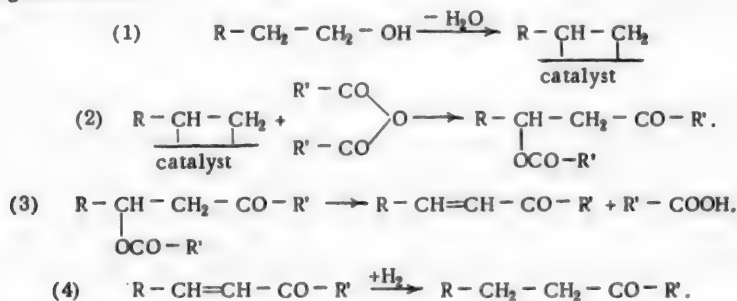
In preceding communications it was shown that reaction of acetic acid with ethyl alcohol [1] and of acetyl chloride with ethyl bromide gives methyl ethyl ketone [2]; acetic acid and n-butyl alcohol give methyl sec-butyl and methyl n-butyl ketones. At the same time a general scheme was put forward for the catalytic synthesis of ketones

[1-3] according to which any two molecules of the type of $R-\overset{\overset{O}{\parallel}}{C}-X$ and $Y-CH_2-CH_2-R'$ must form a ketone over

a catalyst in a specified temperature range in presence of hydrogen. X and Y may be: H, halogens, OH, OR, OCOR, apparently the N(H, R₂) group, etc.

We now continue the investigation and the checking of the theoretical concepts of the mechanism of ketonization advanced previously by one of us [1, 2, 3]. A new method is also submitted for the synthesis of ketones, starting from acetic anhydride and alcohols (ethyl, butyl and isobutyl).

On the basis of the earlier considerations the reaction between an acid anhydride and an alcohol may be represented in the following general form:



Carboxylic acids may here be formed both by hydrolysis of the anhydride with water released in reaction (1), and by decomposition of the keto ester according to (3).

The experimental work confirms this scheme. Actually there were obtained only those reaction products to be expected from the schemes: 1) from acetic anhydride and ethyl alcohol were obtained acetone and methyl ethyl ketone; 2) from acetic anhydride and n-butyl alcohol were obtained acetone, methyl sec-butyl and methyl n-butyl ketones; 3) from acetic anhydride and isobutyl alcohol were obtained acetone and methyl isobutyl ketone.

EXPERIMENTAL

Starting substances. The acetic anhydride had the following constants: b.p. 139.5°, n_D^{20} 1.3900. The ethyl alcohol was dehydrated with copper sulfate (anhydrous). Final concentration of ethanol 99.5% (by weight); b.p. 78.5°, n_D^{20} 1.3615. n-Butyl alcohol had b.p. 117°, n_D^{20} 1.399. Isobutyl alcohol had b.p. 107°, n_D^{20} 1.397. Hydrogen was obtained by the action of sulfuric acid on zinc free from arsenic, and it was purified with a solution of potassium bichromate in sulfuric acid. The catalyst was prepared from chromic oxide and manganese nitrate [4].

Experiments were carried out in an ordinary laboratory catalytic apparatus. The starting mixture was fed at constant speed from an automatic buret. The catalyst (80 ml), consisting of equal parts by weight of chrome-manganese powder and asbestos wool, was placed in a zone of the furnace with approximately identical temperature. The temperature of the electric furnace was adjusted with a laboratory autotransformer and was measured with a thermocouple in a pyrex case placed in the reaction tube. The required volume of hydrogen was measured with a flowmeter. The gases were passed either to atmosphere or to a gasholder for analysis.

The catalyzate was worked up in the following manner: a) preliminary distillation from a Favorsky flask; b) treatment with calcium chloride for removal of water and alcohol; c) fractional distillation in a laboratory

TABLE 1

Experiment No.	Temperature	Feed velocity of mixture (in ml/hour)	Products of reaction (in g)			
			Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
1	400°	15	21.6	—	1.6	—
2	460	15	13.0	—	0.8	—
3	440	25	3.5	—	—	Traces

Note: The amount of mixture in all experiments was 100 ml and the molar ratio of alcohol to anhydride was 1 : 1.

TABLE 2

Experiment No.	Temperature	Reaction products (in g)			
		Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
4	450°	6	1.1	—	—
5	435	10.2	3.2	—	—
6	420	28.0	6.0	—	—
7	405	14.0	5.2	0.8	Traces

Note: In all experiments the amount of mixture was 100 ml; the molar ratio of alcohol to anhydride was 1 : 1; the feed velocity of the mixture was 15 ml/hour.

and attention is drawn to the favorable effect of hydrogen in the ketonization reaction. This role of additions of hydrogen is perceived in the scheme, which indicates that in the first instance vinyl ketones are formed and these are very susceptible to-resinification and polymerization.

The following experiments were carried out in presence of an equimolecular amount of hydrogen in relation to the alcohol. Results of experiments in presence of hydrogen are set forth in Table 2.

As we see from the data of Table 2, in experiments 4-7 the temperature was varied at constant molar ratio of components and constant space velocity. Maximum yield of methyl ethyl ketone was observed at 420°. The results of experiment 7 indicate that at low temperature a part of the acetic anhydride is hydrolyzed by water to acetic acid and does not enter into reaction.

The acetic acid in the reaction products was qualitatively detected by reaction with sodium carbonate and quantitatively determined by titration with caustic alkali solution. Acetaldehyde was identified through the semicarbazone (m.p. 162°). Characteristically the main product of the reaction was acetone, the amount of methyl ethyl ketone being 3 to 5 times smaller.

For establishment of the optimum conditions for formation of methyl ethyl ketone, in the following experiments the space velocity and molar ratio of components were successively changed. Results of these experiments are set forth in Table 3.

As we see from Table 3, the maximum feed velocity of the starting mixture was 40 ml/hour. The optimum molar ratio of components (ethanol and acetic anhydride) was 3 : 1.

Consequently the optimum conditions for methyl ethyl ketone formation are: temperature 420°; molar ratio of ethanol to anhydride 3 : 1; feed velocity of starting mixture of 40 ml/hour. The yield of methyl ethyl ketone was 27.5% of the theoretical calculated on the acetic anhydride. It should be noted that in the case of acetic acid and ethyl alcohol the yield of methyl ethyl ketone may reach over 90% [1].

2. Synthesis of methyl butyl ketones from butyl alcohol and acetic anhydride. All the experiments on synthesis of methyl butyl ketones were carried out in presence of hydrogen. The first experiment was carried out under the optimum conditions for formation of methyl ethyl ketone.

After fractionation of the catalyze and elimination of water and unreacted butyl alcohol, two fractions were

fractionating column. The ketones obtained were identified from their constants and from their semicarbazones and 2,4-dinitrophenylhydrazones. The ketones were quantitatively determined by titration with hydroxylamine hydrochloride in presence of bromophenol blue [5].

1. Synthesis of methyl ethyl ketone from acetic anhydride and ethyl alcohol. Data for experiments in absence of hydrogen are set forth in Table 1.

The data of Table 1 show that the main reaction product is acetone. Methyl ethyl ketone and methyl vinyl ketone were not detected in the catalyzates from any of the three experiments. In experiments 2 and 3 the yield of acetone and acetaldehyde falls regularly. The catalyst was deactivated very quickly. During cleaning of the catalyst tube, a heavy carbonaceous deposit was found upon the catalyst. A similar observation is reported in the literature [6] for copper catalysts

TABLE 3

Experiment No.	Molar ratio of components	Feed velocity of mixture (in ml/hour)	Products of reaction (in g)			
			Acetone	Methyl ethyl ketone	Acetaldehyde	Acetic acid
8	1 : 1	30	23.1	6.8	—	—
9	1 : 1	40	18.0	7.6	—	Traces
10	1 : 1	50	12.0	4.8	0.4	3.1
11	1 : 1	40	8.0	8.0	—	—
12	3 : 1	40	6.1	8.8	—	—
13	4 : 1	40	4.0	6.1	—	—

Note: Amount of mixture in all experiments 100 ml; temperature 420°.

TABLE 4

Experiment No.	Amount of mixture (in ml)	Molar ratio of alcohol to anhydride	Temperature	Products of reaction (in g)				
				Acetone	Methyl sec-butyl ketone	Methyl n-butyl ketone	Acetic acid	Butyraldehyde
2	75	3 : 1	435°	2.1	8.0	2.0	—	16.4
3	75	3 : 1	450	1.4	10.1	3.2	Traces	12.4
4	75	3 : 1	465	0.2	7.8	1.6	1.8	9.1
5	56.5	2 : 1	450	1.9	11.8	3.2	Traces	11.4

Note: Feed velocity of the mixture in all experiments 40 ml/hour.

A series of experiments was carried out to establish the optimum conditions for production of methyl butyl ketones. Results are set forth in Table 4.

The data of Table 4 show that the optimum conditions for catalytic synthesis of methyl butyl ketones are: molar ratio of butyl alcohol and acetic anhydride 2 : 1, space velocity 40 ml/hour, temperature 450°.

The yield of methyl sec-butyl ketone was 60% of the theoretical reckoned on the acetic anhydride; that of methyl n-butyl ketone was 16%.

3. Synthesis of methyl isobutyl ketone from acetic anhydride and isobutyl alcohol. Experiments were carried out in presence of hydrogen. The first experiment was performed under the optimum conditions for production of methyl butyl ketones; from the catalyzate was then isolated isobutyraldehyde with b.p. 64°, n_D^{20} 1.373, and methyl isobutyl ketone, b.p. 117° at 750 mm, n_D^{20} 1.3965, d_4^{20} 0.8038, M_R 29.92, calculated 29.92; semicarbazone m.p. 132.0°, no depression in mixed test; 2,4-dinitrophenylhydrazone m.p. 94°.

According to the reaction scheme the formation of an ester with the structure $(CH_3)_2CCH_2OCOCH_3$ is possible, but this ester was not found when the catalyzate was examined.

It is necessary to point out that the yield of methyl isobutyl ketone was insignificant and amounted to 3.2% of the theoretical reckoned on the acetic anhydride. The yield could not be improved by varying the various conditions of catalysis.

Analysis of the gases. Only those gases were examined which were obtained under optimum conditions for the respective ketones. The unsaturated hydrocarbons, carbon monoxide and carbon dioxide were investigated. Results of gas analysis are set forth in Table 5.

From the data of Table 5 we see that unsaturated hydrocarbons are only obtained when hydrogen is not additionally fed into the system. The yield of carbon dioxide is also characteristic: when the system contains additionally introduced hydrogen, the yield of CO_2 falls 4-5 times, while the yield of carbon monoxide increases. It may be assumed that in the instant of its formation the CO_2 is reduced to CO by hydrogen.

collected: 1st fraction with b.p. 116-118°; 2nd fraction with b.p. 126-129°.

In the first fraction was detected and identified methyl sec-butyl ketone:

B.p. 116-118° at 750 mm
 n_D^{20} 1.3998, d_4^{20} 0.812, M_R 29.87. 2,4-dinitrophenylhydrazone m. p. 107°; a mixed test did not give a melting point depression; semicarbazone m. p. 106° (literature data: m. p. 108 and 106° respectively).

TABLE 5

Results of gas analysis

Number of experimental series		Composition of gas (in vol.-%)		
		Unsaturated hydrocarbons	Carbon monoxide	Carbon dioxide
1	Without hydrogen	4.5	11	8
	With hydrogen	—	17	1.5
2	Without hydrogen	5	21	13
	With hydrogen	—	29	3.5
3	Without hydrogen	—	19.5	1.0
	With hydrogen	5.4	18	4

methyl n-butyl ketone in a yield of 16% reckoned on the acetic anhydride; c) methyl isobutyl ketone from acetic anhydride and isobutyl alcohol in a yield of 3.2%.

4. It was established that only in presence of hydrogen is the catalytic synthesis of saturated ketones from alcohols and acid anhydrides possible.

5. The chrome-manganese catalyst does not deteriorate in presence of hydrogen and does not require regeneration.

SUMMARY

1. It was established that acetic anhydride and ethyl, n-butyl and isobutyl alcohols can serve as components of the ketonization reaction whose mechanism had been proposed by one of us.

2. A new method of synthesis of ketones was developed starting from acid anhydrides and alcohols.

3. The following were synthesized: a) methyl ethyl ketone from acetic anhydride and ethanol in a yield of 27% reckoned on the acetic anhydride; b) methyl sec-butyl ketone from acetic anhydride and butyl alcohol in a yield of 60% and

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Received October 20, 1953

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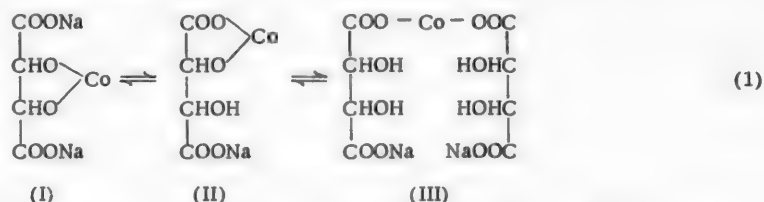
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INFLUENCE OF THE ACIDITY OF THE MEDIUM ON THE COMPOSITION OF TARTRATE COMPLEXES OF COBALT

M. E. Tsimbler

In an investigation of the tartrate complex of cobalt we established [1] that in presence of a complex peptizer (solution of tartrate and alkali) with a ratio of equivalents of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ and NaOH in the range of 1 : 1 to 2 : 1, the complex $\text{Na}_2[\text{CoC}_4\text{H}_2\text{O}_6]$ is formed. When studying the tartrate complex of bismuth, copper and cadmium, we satisfied ourselves that, depending on the concentration of tartrate and alkali, the composition of the complex changes. With increasing concentration of tartrate the formation of complexes proceeds at the expense of the carboxyl and hydroxyl groups of the tartrate.

Reaction of solutions of sodium tartrate with salts of cadmium and copper gives the complexes $\text{Na}_2[\text{Me}(\text{C}_4\text{H}_4\text{O}_6)_2]$, where $\text{Me} = \text{Cd}^{++}$ or Cu^{++} ; consequently complex formation proceeds at the expense of the carboxyl groups [1]. Hence, by analogy, we may suggest that with falling pH of the solution the reaction of formation of tartrate complexes of cobalt ought to proceed according to the scheme:



On this basis we should expect that with falling concentration of NaOH in the complex peptizer, the formation of the complex ought to proceed at the expense of one carboxyl and one hydroxyl group of the tartrate, or only at the expense of its carboxyl groups. We decided that it was of interest to verify this hypothesis experimentally. The complex (II) was prepared from solutions with a ratio of equivalents of tartrate and caustic alkali in the range of 4 : 1 to 8 : 1. We determined the composition of the resultant complexes by the previously developed method, whose main features are outlined below.

The complex is precipitated by running 20-25 ml 96% alcohol into the solution. The precipitate is quickly filtered and washed with alcohol until free from OH^- and SO_4^{--} ions. The wet precipitate is then transferred to a porcelain dish, dried to constant weight at 105° and analyzed.

A weighed amount of 0.18-0.2 g precipitate is carefully burned and ignited in a porcelain crucible (for determination of the content of volatiles). The solid is transferred to a beaker, treated with hot water, and left to stand; the solution is then filtered into a flask. This operation is repeated until the solution is neutral to phenolphthalein. After being made alkaline, the residue in the beaker is transferred to a filter. The amount of alkali in the filtrate is determined and recalculated for sodium.

The residue and filter are transferred to a beaker and dissolved with heating in 2 N sulfuric acid. Since the solid dissolves very slowly, a little concentrated sulfuric acid is added to the solution which is heated and then stood for 12 hours. The solution is then evaporated down and the cobalt is determined [2].

From the determination of the composition (we omit numerical data) it could be concluded that in the compounds formed the amount of sodium decreases while that of cobalt increases in comparison with the complex (I) for which was calculated (%): Na 18.3; Co 23.4. Thus, for example, when using a complex peptizer with an 8 : 1 ratio of equivalents the following contents were found: Na 11.61%; Co 24.55%. For the complex $\text{Na}[\text{CoC}_4\text{H}_3\text{O}_6]$ were calculated (%): Na 10.04; Co 25.74. From a comparison of these figures we can conclude that under these conditions equilibrium (1) is shifted in the direction of formation of the complex $\text{Na}[\text{CoC}_4\text{H}_3\text{O}_6]$. It was impossible to separate complex (II). Consequently with participation of a complex peptizer in the solution two complexes (I) and (II) are formed, but the relative amount of complex (II) increases with decreasing concentration of NaOH in the complex peptizer.

For the preparation of the complex $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2]$ (III), formed at the expense of only the carboxyl groups,

TABLE 1

Taken (in ml)		Weight of dry precipitate (in g)	0.1 N HCl used (ml)	Found (%)	
0.5 N $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	0.5 N $\text{Co}(\text{NO}_3)_2$			Na	Co
25	5	0.2046	9.60	10.79	16.86
20	4	0.1980	9.05	10.51	16.95

TABLE 2

Taken (in ml)		Weight of dry precipitate (in g)	0.1 N HCl used (ml)	Found (%)	
0.5 N $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	0.5 N CoSO_4			Na	Co
20	4	0.2024	10.05	11.42	11.62
20	4	0.2232	10.95	11.28	14.54

4-5 ml 0.5 N solution of CoSO_4 or $\text{Co}(\text{NO}_3)_2$ was run into 20-25 ml 0.5 N solution of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$. Analysis was performed as above. Results obtained are set forth in Table 1.

From an examination of the data of this table we see that complexes (III) and (II) are present in the compounds formed. Found %: Na 10.65; Co 16.90; $\text{C}_4\text{H}_4\text{O}_6^{2-}$ 72.45. $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2]$. Calculated %: Na 11.49; Co 14.70; $\text{C}_4\text{H}_4\text{O}_6^{2-}$ 73.81. The presence in the isolated precipitates of an insignificant amount of complex (II) is evidently to be explained by the fact that OH^- ions are present in the $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ solution, due to hydrolysis, and these make possible the formation of a small amount of $\text{C}_4\text{H}_3\text{O}_6^{3-}$ anions:



With the objective of completely suppressing the formation of $\text{Na}[\text{CoC}_4\text{H}_3\text{O}_6]$ and of obtaining solely $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2]$, we decided to lower the pH of the sodium tartrate solution; for this we carried out experiments using a solution of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ brought to acid reaction in presence of methyl red indicator (Table 2). The composition was determined by the previously described method with the following modification: the complex was brought down with 96° alcohol and washed with dilute 70° alcohol until free from SO_4^{2-} . The reason for the modification was that in presence of salts (obtained on neutralizing $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$) the addition of 96° alcohol brings down unreacted tartrate together with the complex. The data of Table 2 show that the formula of the complex formed is $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2]$.

SUMMARY

1. The reaction of formation of tartrate complexes of cobalt in presence of a solution of a complex peptizer proceeds according to scheme (1). With decreasing concentration of the NaOH solution of the complex peptizer, the equilibrium is shifted from left to right in the equation $[\text{CoC}_4\text{H}_2\text{O}_6]^- + \text{H}^+ \rightleftharpoons [\text{CoC}_4\text{H}_3\text{O}_6]^-$.

2. Reaction of solutions of $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ (pH 4.4) with cobalt salts gives the tartrate complex $\text{Na}_2[\text{Co}(\text{C}_4\text{H}_4\text{O}_6)_2]$.

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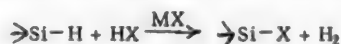
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STUDY OF THE REACTION OF TRIALKYSILANES WITH ALCOHOLS

SYNTHESIS OF TRIALKYLALKOXY-SILANES AND THEIR PHYSICAL PROPERTIES

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One of the principal differences between the chemistry of silicon and the chemistry of carbon is the very much greater reactivity (which is also specific) of the Si-H bond in comparison with the C-H bond. Thus, for example, the Si-H bond is readily cleaved by water [1-8], alcohols [9-20], ammonia [21, 22, 25] and amines [21-24, 35] in presence of the suitable bases - hydroxides, alcoholates and amides of alkali metals - according to the general scheme:



(X = OH, OR, NH₂, NHR, NR₂; M = Li, Na, K).

The Si-H bond is also cleaved by water in presence of ammonia [25] or organic bases like piperidine [14, 26] or tetraalkylammonium hydroxides [27]. Cleavage of the Si-H bond also takes place under the action of alcoholic solutions of ammonia [15]. By contrast, the Si-H bond exhibits adequate stability towards dilute mineral acids and is completely inert to pure water and alcohols.

All these reactions of substitution of the hydrogen atom linked to silicon have no analogy in organic chemistry. They occur because the Si-H bond is polarized in a different direction to the C-H bond due to silicon possessing a lower electron affinity (0.60 eV) than hydrogen (0.76 eV), whereas carbon possesses an electron affinity (1.37 eV) greater than that of hydrogen. Due to this, the hydrogen atom bound to silicon carries a negative charge and is susceptible to cleavage in the form of hydride ion. All this indicates that, when drawing an analogy between the chemistry of silicon and the chemistry of carbon, we ought to compare the Si-H bond not with the C-H bond but with the similarly polarized carbon - halogen bond.

The present work is devoted to a study of the reaction of trialkylsilanes with alcohols. All the cited literature studies which report reactions at the Si-H bond were carried out solely with primary alcohols. In not one of these investigations was an attempt made to study the influence on the course of alkoxylation of the Si-H bond of the structure of the alcohol and of the nature of the alkaline catalyst. Only in an investigation by Price [9] was a study made of the influence on the speed of reaction of the Si-H bond with alcohols of the substituents at the silicon atom. In this investigation, however, the final products of reaction were not isolated.

We have shown that trialkylsilanes R₃SiH (R = C₂H₅, n-C₃H₇, n-C₄H₉) react with primary, secondary and tertiary alcohols in presence of alkoxides of alkali metals; in the case of primary and secondary alcohols the reaction is effected by simple boiling of the mixture of trialkylsilane and alkali metal solution (molar ratio of the latter to the original R₃SiH is 4-25%) in double the theoretical amount of the corresponding anhydrous alcohol. The yields of trialkylalkoxysilanes are lowered by the presence of water in the original alcohol or by the use of alcoholic solutions of hydroxides of alkali metals due to formation of products of hydrolysis - hexaalkyldisiloxanes. The progress of the reaction is readily followed from the volume of hydrogen formed, which is usually separated in the theoretical amount. The trialkylalkoxysilanes formed in the reaction whose yields are 80-90%, are separated by fractional distillation of the reaction mixture at the ordinary or reduced pressure.

In the absence of catalysts the trialkylsilanes do not react with alcohols. Thus, for example, on boiling triethylsilane with anhydrous ethyl alcohol in a quartz vessel in the course of 24 hours, no reaction whatever was observed.

The experimental data obtained in the present work permit us to recognize the following regularities in the reaction of trialkylsilanes with alcohols.

The velocity of reaction of trialkylsilanes with alcohols decreases with increasing length of the alkyl radicals R in R₃SiH. Thus, for instance, the theoretical amount of hydrogen in the reaction of n-butyl alcohol in presence of 8-mole-% C₄H₉ONa with triethylsilane comes off after 4 hours, with tri-n-propylsilane after 5 hours, and with tri-n-butylsilane after 10 hours.

With increasing length of the alcoholic radical the speed of reaction of trialkylsilanes with primary normal alcohols is slightly lowered. Owing to the considerable steric hinderance, isobutyl alcohol reacts with triethylsilane more slowly than isoamyl alcohol, while the latter reacts with the same velocity as normal alcohols.

A profound influence upon the reaction of trialkylsilanes with alcohols is exerted by the nature of the alkali metal alkoxides. With increasing atomic number of the alkali metal (from lithium to rubidium), the velocity of reaction of trialkylsilanes with alcohols rises, while the yields of the resultant trialkylalkoxysilanes fall. Increased

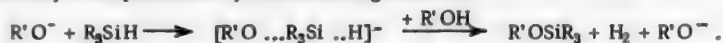
concentration of alkoxide in the reaction mixture leads to a certain increase in the reaction velocity and in the yields of trialkylalkoxysilanes. In addition, the nature of the alkali metal alkoxide affects the reaction of trialkylsilanes with alcohols at normal pressure in the following manner. In presence of lithium alkoxides trialkylsilanes react only with primary alcohols. In presence of sodium alkoxides trialkylsilanes react not only with primary but also with secondary alcohols. In the latter case, however, the reaction often proceeds slowly and does not proceed to the end, while the yields of trialkyl-sec-alkoxysilanes are relatively low. When using potassium alkoxides as catalysts, trialkylsilanes react substantially equally well with primary and secondary alcohols. Tertiary alcohols and phenols do not react with trialkylsilanes in presence of the corresponding alkoxides of lithium, sodium and potassium. Mercaptans likewise do not react with trialkylsilanes in presence of mercaptides of alkali metals. In presence, however, of alkoxides of rubidium, trialkylsilanes also react with tertiary alcohols. It must be admitted that in the latter case the reaction does not proceed to the end, and the yield of trialkyl-tert-alkoxysilanes is low (of the order of 10%).

When the reaction is performed in an autoclave at 200-210° in presence of the corresponding sodium alkoxides, the trialkylsilanes smoothly react not only with primary and secondary but also with tertiary alcohols. In this way we synthesized a series of trialkyl-tert-alkoxysilanes in a yield of 80-85%. The synthesis of these compounds is especially interesting since it is difficult to prepare trialkyl-tert-alkoxysilanes by the usual methods. In particular we failed in an attempt to obtain triethyl-tert-butoxysilane by transesterification of triethylmethoxysilane with tert-butyl alcohol in presence of sodium tert-butoxide.

On the other hand the transesterification of triethylmethoxysilane with n-butyl and isobutyl alcohols in presence of the corresponding sodium butoxides permitted us to obtain the n-butoxy and isobutoxy derivatives in 80-90% yield. Transesterification of triethylmethoxysilane with sec-butyl alcohol proceeds slowly, due to which the yield of triethyl-sec-butoxysilane is low.

We also found that triethylsilane reacts with ethyl alcohol also in the absence of an alkaline catalyst when the reaction is carried out in an autoclave at 200°, triethylethoxysilane being formed in a yield of 88%. We think it probable, however, that in this case metallic copper or iron were catalysts of the reaction, since at the end of the reaction the copper obturator and the walls of the autoclave were found to be corroded. This inference is also supported by the fact that triethylsilane reacts with ethyl alcohol in presence of active copper powder on boiling at the ordinary pressure. In this case, however, the yield of triethylethoxysilane is low (11%) and the reaction proceeds slowly.

The reaction of trialkylsilanes with alcohols (and water) which is catalyzed by alkoxides of alkali metals is undoubtedly an ionic one. This is confirmed by the fact that in the absence of alcohols the individual alkoxides (and also the anhydrous hydroxides) of alkali metals do not react with trialkylsilanes. Our experimental data conclusively prove that the reaction of trialkylsilanes with alcohols is a bimolecular nucleophilic substitution ($S_N 2$, according to Ingold and Hughes) whose mechanism may be represented by the following scheme:



This scheme shows that the attack of the electron-donating alkoxyl ion on the positively polarized silicon atom leads to cleavage of the hydride ion which quickly combines with the alcohol with liberation of a molecule of hydrogen. The latter stage leads to liberation of the alkoxyl ion. The above scheme explains the mechanism of the catalytic action of alkali metal alkoxides which bring about an increase in the concentration of basic OR^- .

It is most probable that entering into the composition of the complex $[R'O \cdots R_3Si \cdots H]^-$, formation of which is hindered by H^+ ions, are a molecule of alcohol together with the alkoxyl ion, so that both of the above-indicated stages proceed simultaneously.

Consequently the reaction velocity, depending on the concentration of OR^- ions (and on the lengths of ions $R'OH_2^+$), is determined by the dissociation constant and by the concentration of alkoxide of the alkali metal and by the autoprotolysis constant of the alcohol.

Increase in the size of the alkyl radicals in the trialkylsilanes, leading to a fall in the velocity of their reaction with alcohols, creates a stronger field of force, due to which the energy barrier for penetration of the alkoxyl ions to the silicon atom becomes larger, whereas the stability of the Si-H bond remains substantially unchanged with increasing size of the alkyl radicals in trialkylsilanes. This is confirmed by infrared spectroscopic data obtained in the present investigation which show that the absorption band corresponding to the valence vibration of Si-H in three trialkylsilanes R_3SiH ($R = C_2H_5$, $n-C_3H_7$ and $n-C_4H_9$) is identical ($2106 \pm 2 \text{ cm}^{-1}$)*. This frequency of the Si-H bond in trialkylsilanes is smaller than in trichlorosilane (2257 cm^{-1}) and in tribromosilane (2236 cm^{-1}),** which reflects the lower

* In the literature are given the vibration frequency of Si-H in trimethylsilane [28] and methyldiallylsilane [29] determined by Raman spectrography; the respective values are 2118 and 2117 cm^{-1} .

** Data for tribromosilane were obtained by Raman spectrography [30].

TABLE 1

Autoprotolytic constant (pK) of compounds containing a mobile hydrogen at 25° [32]

Formula	pK	Formula	pK
H ₂ SO ₄	3.0	CH ₃ OH	16.7
HCOOH	6.3	C ₂ H ₅ OH	19.0
CH ₃ COOH	12.6	NH ₃	22 (-34°)
HOH	14.0		

the alkoxyl ion (particularly if it is solvated). These steric hindrances, associated with increasing branching of the alcoholic radical, evidently are many times greater than the accompanying increase of basicity of the alcohol (due to the inductive effect of the alkyl groups) which promotes the alkoxylation of trialkylsilanes.

Alcohols which do not contain sterically-hindering radicals but which possess acidic properties (phenols), as well as water, organic acids [36] and mercaptides, do not react with trialkylsilanes. Thus, for example, we failed to observe a reaction of triethylsilane with phenol when boiled in presence of phenates of lithium, sodium or potassium. Similarly no reaction occurred between triethylsilane and organic acids in presence of their alkali metal salts.

Triethylsilane is completely unchanged after prolonged boiling with water or with 1 N aqueous NaOH and KOH, in which it is insoluble. Furthermore, the reaction of triethylsilane with aqueous solutions of NaOH or KOH does not proceed even in a homogeneous medium obtained by addition of dioxane (but not of alcohol). Such a difference in reactivity of trialkylsilanes with alcohols on the one hand and with water, phenols, mercaptans and organic acids on the other is explained by the higher autoprotolytic constant of alcohols in comparison with water, phenols, mercaptans and carboxylic acids (see Table 1). As further evidence in support of this conclusion, methyl alcohol, which possesses a lower autoprotolytic constant than ethyl alcohol, differs from the latter in not reacting with silane in presence of lithium alkoxide [31]. Ammonia, possessing a very high autoprotolytic constant, on the contrary reacts with triethylsilane in presence of potassium amide even at -35° [35].

The influence of the nature of the cation in the alkali metal alkoxide catalyzing the reaction of trialkylsilanes with alcohols is associated with the rise in atomic number of the metal, i.e., in passing from lithium to rubidium there is a considerable rise in the degree of ionization (alkalinity), leading to a rise in the concentration of alkoxyl ions and, consequently, to a rise in reaction velocity.

All the foregoing considerations indicate that reactions of trialkylsilanes with alcohols and other compounds containing mobile hydrogens (water, ammonia, amines), which proceed according to the S_N2 type, are promoted by the fall of concentration of H⁺ ions which takes place with rise of the autoprotolytic constant of the reactant (solvent) and with rise of concentration of negative ions (R'O⁻ in the case of alcohols) and which is intensified with increasing atomic number of the alkali metal whose derivatives serve as the catalyst.

In the course of the present investigation we synthesized 28 pure trialkylalkoxysilanes and determined their physical properties, which are set forth in Table 2; 27 of these compounds have not previously been reported in the literature. Triethylphenoxysilane was prepared by reaction of triethylsilane with phenol in presence of iodine and aluminum iodide by the method which we developed for synthesis of trialkylacyloxysilanes [36].

The reaction of trialkylsilanes with alcohols studied by us is a convenient general method of alkoxylation of the Si-H bond. This method is distinguished by its simplicity and by the high yields of alkoxy derivatives, which are easily separated in the pure form owing to the absence of any secondary reaction products.

EXPERIMENTAL

Starting components

Trichlorosilane was obtained in a yield of about 75% by the reaction of hydrogen chloride with silicon or with high-percentage ferrosilicon at 290-300°. The HSiCl₃ purified in a column had b.p. 31.8° (760 mm).

Triethylsilane, tri-n-propylsilane and tri-n-butylsilane were prepared by reaction of the corresponding alkyl magnesium chlorides with trichlorosilane and purified by distillation in a column (tributylsilane was distilled in vacuum). Their yields, physical properties and analyses are set forth in Table 3.

The starting alcohols were purified by distillation in a column and possessed constants identical with the best literature data [33]. Alcohols with b.p. below 100° were previously freed from water by boiling with metallic calcium. Tert-butyl alcohol was repeatedly frozen after distillation.

stability of the Si-H bond in trialkylsilanes (due to the influence of the halogen atoms, the polarization of the Si-H bond in trihalogenosilanes, and consequently also their susceptibility to reactions of nucleophilic substitution, is sharply reduced).

The sharp drop in velocities of reactions of trialkylsilanes with alcohols on passing from primary to secondary and, in particular, to tertiary alcohols, as also the small decrease of reaction velocities with increasing length of the alcohol radical or on passing from normal to iso alcohols, are accounted for by the same steric hindrances to nucleophilic attack of the silicon atom by

TABLE 2

Trialkylalkoxysilanes R_3SiOR

Trialkylalkoxy silane No.	R_3SiOR	Boiling point*	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20} - n_C^{20}$	γ^{20}
1	$(C_2H_5)_3SiOCH_3$	141.5°	760	0.8203	1.4129	0.0081	21.53
2	$(C_2H_5)_3SiOC_2H_5$	154.0	760	0.8160	1.4140	0.0082	22.09
3	$(C_2H_5)_3SiOCH_2CH_2CH_3$	175.3	760	0.8159	1.4177	0.0076	22.88
4	$(C_2H_5)_3SiOCH(CH_3)_2$	166.5	760	0.8079	1.4133	0.0083	20.84
5	$(C_2H_5)_3SiOCH_2CH_2CH_2CH_3$	193.8	760	0.8186	1.4210	0.0074	23.00
6	$(C_2H_5)_3SiOCH_2CH(CH_3)_2$	186.3	760	0.8129	1.4184	0.0084	22.35
7	$(C_2H_5)_3SiOCH(CH_3)CH_2CH_3$	187.0	760	0.8188	1.4203	0.0076	22.66
8	$(C_2H_5)_3SiOC(CH_3)_3$	178.5	760	0.8115	1.4181	0.0077	21.34
9	$(C_2H_5)_3SiOCH_2(CH_2)_3CH_3$	213.8	760	0.8212	1.4250	0.0083	23.46
10	$(C_2H_5)_3SiOCH_2CH_2CH(CH_3)_2$	205.7	760	0.8176	1.4237	0.0072	23.25
11	$(C_2H_5)_3SiOC(CH_3)_2C_2H_5$	201.2	760	0.8253	1.4270	0.0075	23.25
12	$(C_2H_5)_3SiOCH_2(CH_2)_4CH_3$	231.3	760	0.8230	1.4281	0.0081	25.23
13	$(C_2H_5)_3SiOCH_2(CH_2)_5CH_3$	248.0	760	0.8255	1.4310	0.0080	24.99
14	$(C_2H_5)_3SiOCH_2(CH_2)_6CH_3$	267.0	760	0.8267	1.4332	0.0076	25.40
15	$(C_2H_5)_3SiOCH_2CH_3(CH_2)_6CH_3$	256.3	760	0.8259	1.4327	0.0075	25.50
16	$(C_2H_5)_3SiOC_6H_{11}$	237.1	760	0.8769	1.4481	0.0080	27.12
17	$(C_2H_5)_3SiOC_6H_5$	243.6	760	0.9374	1.4880	0.0134	29.66
18	$(C_2H_5)_3SiOCH_2C_6H_5$	262.6	760	0.9319	1.4852	0.0125	28.64
19	$(C_2H_5)_3SiOCH_2CH_2OC_2H_5$	210.9	760	0.8650	1.4237	0.0080	25.06
20	$(C_2H_5)_3SiOCH_2CH_2NH_2$	201.6	760	0.8749	1.4385	0.0082	26.94
21	$(n-C_3H_7)_3SiOCH_2(CH_2)_2CH_3$	102.5	9	0.8203	1.4300	0.0075	24.66
22	$(n-C_3H_7)_3SiOCH_2CH(CH_3)_2$	90.5	5	0.8140	1.4280	0.0077	23.59
23	$(n-C_3H_7)_3SiOCH_2CH_3C_2H_5$	91.5	6.5	0.8204	1.4289	0.0079	24.11
24	$(n-C_3H_7)_3SiOC(CH_3)_3$	84.5-85.0	6	0.8151	1.4280	0.0075	23.48
25	$(n-C_4H_9)_3SiOCH_2(CH_2)_3CH_3$	123.5-124.0	5	0.8285	1.4370	0.0078	25.44
26	$(n-C_4H_9)_3SiOCH_2CH(CH_3)_2$	121.0	6	0.8220	1.4351	0.0075	24.27
27	$(n-C_4H_9)_3SiOCH(CH_3)C_2H_5$	130.0	9	0.8229	1.4362	0.0076	25.30
28	$(n-C_4H_9)_3SiOC(CH_3)_3$	120.5	7	0.8199	1.4350	0.0081	24.89

* Subscripts in formula illegible in original.

TABLE 3

Properties of Trialkylsilanes R_3SiH

R_3SiH	Yield (in % of theoretical)	Boiling point	Pressure (in mm)	d_4^{20}	n_D^{20}	$n_F^{20} - n_C^{20}$	γ^{20}	Molecular wt.		Si (in %)	
								Calcu- lated	Found	Calcu- lated	Found
$(C_2H_5)_3SiH$	70	107.7°	760	0.7309	1.4121	0.0081	20.52	116.28	113.4	24.14	24.00
(iso.- C_3H_7) $_3SiH$	66.7	173.2	760	0.7580	1.4272	0.0082	22.98	158.36	157.4	17.72	17.62
(iso.- C_4H_9) $_3SiH$	65.1	88-89	5	0.7795	1.4380	0.0083	24.86	200.43	199.0	14.00	13.85

The metallic lithium, sodium, potassium and rubidium were the commercially pure preparations.

EXPERIMENTAL PROCEDURE

All the reactions of trialkylsilanes with alcohols at the ordinary pressure were carried out in two-necked, round-bottomed flasks with a volume of 100 ml, equipped with reflux condenser and thermometer. The top end of the condenser was joined to a gasholder for collection of hydrogen through a Tishchenko bottle filled with concentrated sulfuric acid. Reactions under pressure were carried out in a 225 ml steel autoclave.

Syntheses were effected by heating a mixture of 0.1 mole trialkylsilane with twice the theoretical amount of alcohol in which had previously been dissolved 0.1-1 g of the particular alkali metal. Heating was continued until hydrogen ceased to come off. The excess of alcohol and the trialkylalkoxysilane formed were dissolved off

TABLE 2 Continued

Molecular weight		Analysis (in %)						Yield of R_3SiOR' (in %)		
Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	in presence of		
								LiOR'	NaOR'	KOR'
146.30	145.6, 144.2	57.48	56.99, 56.94	12.34	12.36, 12.30	19.19	19.01, 19.03	—	92.7	93.0
160.33	160.0, 158.4	59.94	59.77, 59.73	12.58	12.60, 12.58	17.50	17.30, 17.38	46.8	83.0	90.1
174.36	173.4, 172.3	62.04	61.79, 61.81	12.72	12.86, 12.74	16.10	15.92, 16.01	—	83.0	—
174.36	172.9, 171.3	62.04	61.93, 62.04	12.72	12.89, 12.72	16.10	15.91, 16.00	0	14.3	80.0
188.38	187.7, 185.9	63.76	63.54, 63.63	12.84	12.82, 12.99	14.88	14.71, 14.71	—	85.6	—
188.38	188.1, 186.4	63.76	63.49, 63.50	12.84	12.93, 12.92	14.88	14.69, 14.81	—	81.3	—
188.38	188.2, 186.1	63.76	63.61, 63.19	12.84	12.99, 12.86	14.88	14.68, 14.79	0	8.0	90.3
188.38	186.3, 185.4	63.76	—	12.84	—	14.88	14.68, 14.69	0	0; 84.0*	0**
202.41	200.2, 199.1	65.39	64.77, 64.99	12.96	13.00, 13.09	13.87	13.60, 13.68	—	86.8	—
202.41	201.3, 201.6	65.39	65.07, 65.09	12.96	13.00, 13.12	13.87	13.66, 13.77	—	81.4	—
202.41	199.0, 198.6	65.39	—	12.96	—	13.87	13.62, 13.69	0	0; 85.4*	0
216.43	215.4, 211.4	66.59	65.98, 66.19	13.04	13.10, 13.00	12.97	12.81, 12.73	—	88.9	—
230.46	228.8, 227.1	67.75	67.50, 67.28	13.12	13.28, 13.19	12.18	11.88, 11.99	—	91.4	—
244.49	244.2, 243.8	68.35	67.85, 67.88	13.19	13.30, 13.21	11.47	11.31, 11.43	—	81.0	—
244.49	242.8, 241.9	68.35	67.95, 67.91	13.19	13.20, 13.26	11.47	11.27, 11.32	0	—	80.5
214.42	214.1, 213.0	67.22	66.79, 66.84	12.22	12.30, 12.30	13.08	12.92, 12.97	0	—	81.0
208.37	206.4, 206.4	69.16	68.73, 68.88	9.67	9.79, 9.79	13.47	13.26, 13.29	0	0	0***
222.40	221.3, 222.7	70.21	69.85, 70.01	9.97	9.96, 10.01	12.61	12.40, 12.52	—	80.9	—
204.38	200.8, 201.7	53.87	—	11.84	—	13.73	13.60, 13.69	—	92.3	—
175.35	172.0, 172.8	54.82	—	12.07	—	16.00	15.82, 15.87	—	84.9	—
230.46	229.1	67.75	—	13.12	—	12.18	11.99, 12.03	—	87.7	—
230.46	228.5	67.75	—	13.12	—	12.18	11.99, 12.01	—	85.4	—
230.46	226.9	67.75	—	13.12	—	12.18	11.94, 12.02	—	79.9	—
230.46	229.7	67.75	—	13.12	—	12.18	11.98, 11.99	—	82.5*	—
272.54	270.6	70.51	—	13.31	—	10.29	10.05, 10.17	—	87.6	—
272.54	269.2	70.51	—	13.31	—	10.29	10.09, 10.11	—	84.6	—
272.54	270.6	70.51	—	13.31	—	10.29	10.05, 10.05	—	80.8	—
272.54	272.0	70.51	—	13.31	—	10.29	10.09, 10.13	—	80.0*	—

* In autoclave at 210°. ** 6.8% in presence of $RbOC(CH_3)_3$. *** In presence of AlH_3 . Yield 80.8%.

from the metal alkoxide, after which the trialkylalkoxysilane was purified by distillation in a column with an efficiency of 10-12 theoretical plates.

The method of determination of the physical constants and the accuracy of their determination are described in one of our papers [34]. For determination of the constants, all the substances were redistilled in a column, the middle cuts with constant boiling points being collected.

The infrared spectra of the trialkylsilanes were plotted in the region of the principal frequency of the Si-H vibration in a Perkin-Elmer 12B spectrophotometer fitted with a LiF prism. The spectral width of the slit was of the order of 3 cm^{-1} . The thickness of the layer was of the order of 0.007 mm. Electrooptical intensification.*

Silicon was determined by mineralization of the sample to SiO_2 with a mixture of oleum and fuming nitric acid [34]. Carbon and hydrogen were determined by combustion in a tube over copper oxide in presence of a mixture of lead acetate and potassium dichromate. The silica fume in the combustion tube was trapped by a plug of calcined asbestos inserted in the tube.

Below we give details of some of the more typical experiments.

Synthesis of triethylmethoxysilane. 31.8 g triethylsilane was added to a solution of 0.1 g sodium in 19.2 g methanol. The reaction mixture was boiled until hydrogen had entirely ceased to come off (2.5 hours); the amount of hydrogen was 8 liters. The reaction product was distilled off from the sodium methoxide and distilled in a column. Yield of triethylmethoxysilane with b.p. 141.4-141.8° (759 mm) 40.7 g (92.7%).

* The infrared spectra were plotted by M.O. Bulanin, to whom the authors express their gratitude.

Synthesis of triethylethoxysilane.* a) To a solution of 0.1 g potassium in 9.2 g ethyl alcohol was added 11.6 g triethylsilane. The reaction starts even in the cold (hydrogen evolution). After 2 hours' heating of the reaction mixture at the boil, 2.3 liters hydrogen had come off. After distillation from the potassium ethoxide, the reaction product was distilled in a column. Yield of triethylethoxysilane with b.p. 153.0-153.7° (751 mm) 14.5 g (90.1%).

b) 11.6 g triethylsilane and 20.0 g ethyl alcohol were heated in an autoclave at 200° for 20 hours. After this period the pressure in the autoclave had reached 27 atm. After cooling the autoclave to room temperature, the internal pressure remained at 8 atm. The volume of hydrogen evolved during the reaction and passing into the gasholder was 2.2 liters. After the reaction had been carried out, the steel walls of the autoclave and the copper obturator were found to be corroded. Distillation of the reaction mixture in a column gave 14.0 g triethylethoxysilane with b.p. 152.0-153.6° (751.3 mm), i.e., 87.5% of the theoretical yield.

c) A mixture of 11.6 g triethylsilane, 9.2 g 96% ethyl alcohol and 1.5 g NaOH was heated to the boil for 3 hours. After this period 1.5 liters hydrogen had come off. Distillation of the reaction mixture in a column gave 6.4 g (40%) of triethylethoxysilane with b.p. 152.5-154.0°.

d) A mixture of 11.6 g triethylsilane and 9.2 g ethyl alcohol was boiled for 24 hours in a quartz flask. Evolution of hydrogen was not observed and the weight of triethylsilane remained unchanged.

e) A mixture of 11.6 g triethylsilane and 9.2 g ethyl alcohol was boiled in a quartz flask for 18 hours in presence of 1.75 g active copper powder. During this period 0.25 liter hydrogen was evolved. Distillation of the reaction mixture in a column gave 1.6 g triethylethoxysilane with b.p. 153.5-153.9° (747.6 mm). Treatment of the lower boiling fractions with water gave 8.3 g unchanged triethylsilane with b.p. 107.9-108.2° (747.6 mm).

Reaction of triethylsilane with water and aqueous alkalis

On boiling 11.6 g triethylsilane with 15 ml distilled water or with 15 ml 1 N KOH or NaOH for 24 hours, no reaction at all was observed. All the triethylsilane remained unchanged. On boiling a homogeneous mixture of 11.6 g triethylsilane, 3.6 g distilled water and 10 ml dioxane in which was dissolved 0.1 g metallic sodium, no evolution of hydrogen was observed in the course of 17 hours.** After treatment of the reaction mixture with water, 10.2 g unchanged triethylsilane was isolated. A similar result was obtained on replacing the sodium by 0.2 g metallic potassium.

Synthesis of triethylisopropoxysilane. To a solution of 1.0 g potassium in 12.0 g isopropyl alcohol was added 11.6 g triethylsilane. The mixture was heated at the boil for 3 hours, during which period 2.3 liters hydrogen came off. After distilling off from potassium isopropoxide, the reaction mixture was distilled in a column to give 14.0 g (80%) triethylisopropoxysilane with b.p. 166.5-167.0° (769.2 mm). A reduction in the amount of potassium leads to a fall in yield of triethylisopropoxysilane.

Reaction of 11.6 g triethylsilane with a solution of 0.8 g Na in 12.0 g isopropyl alcohol at the boil for 5 hours led to release of only 0.2 liter hydrogen. The yield of triethylisopropoxysilane was 2.5 g (14.3%). The greater part (10.0 g) of the triethylsilane did not enter into reaction and remained unchanged. When the reaction was carried out with a smaller amount of sodium (0.1 g), no triethylisopropoxysilane was formed under the conditions mentioned, and the whole of the triethylsilane remained unchanged.

On prolonged boiling of 11.6 g triethylsilane with a solution of 0.2 g lithium in 12.6 g isopropyl alcohol, no hydrogen was evolved and no triethylisopropoxysilane was formed. The whole of the original triethylsilane remained unchanged.

Synthesis of triethylisobutoxysilane. To a solution of 0.3 g sodium in 14.8 g isobutyl alcohol was added 11.6 g triethylsilane. After 2 hours' heating of the reaction mixture at the boil, the evolution of hydrogen ceased (its volume was then 1 liter). On adding a further 0.5 g sodium to the reaction mixture and continuing heating for 3 hours, a further 1.3 liters hydrogen came off (making 2.3 liters in all). Distillation in a column gave 15.2 g (81.3%) triethylisobutoxysilane with b.p. 184.5-186.0° (754.2 mm).

Synthesis of triethyl-tert-butoxysilane. A solution of 0.1 g sodium in 14.8 g tert-butyl alcohol and 11.6 g triethylsilane were heated in an autoclave at 200-205° for 20 hours. The maximum pressure was 25 atm at 200° and 5 atm. at room temperature.

The evolved hydrogen occupied a volume of 2.3 liters when transferred to the gasholder. Distillation of the

* When studying the reactions of triethylsilane with ethyl alcohol, we found that these two substances form a constant boiling mixture with b.p. 73.0-74.0° containing about 50% triethylsilane.

** An alcoholic solution of C_2H_5ONa by contrast smoothly reacts with triethylsilane in presence of an equal volume of dioxane.

reaction mixture gave 15.8 g triethyl-tert-butoxysilane with b.p. 176.7-178.2° (754.6 mm). No hydrogen evolution was observed on prolonged heating of triethylsilane with solutions of sodium or potassium in tert-butyl alcohol at atmospheric pressure, and the whole of the triethylsilane remained unchanged. Boiling for 8 hours of 11.6 g triethylsilane with a solution of 1.0 g rubidium in 14.8 g tert-butyl alcohol led to evolution of 0.15 liter hydrogen. The yield of triethyl-tert-butoxysilane with b.p. 177.2-178.4° (762.1 mm) and n_D^{20} 1.4180 was 1.3 g (6.8%). Reaction of triethylsilane with tert-butyl alcohol in presence of aluminum iodide is accompanied by release of hydrogen but leads to formation of hexaethyldisiloxane.

Synthesis of triethyl-n-heptoxysilane. To a solution of 0.3 g sodium in 23.2 g n-heptyl alcohol was added 11.6 g triethylsilane. The reaction mixture was heated at the boil for 3 hours. During this period 2.3 liters hydrogen was given off. Yield of triethyl-n-heptoxysilane with b.p. 247.3-247.6° (752.0 mm), 21.2 g (91.4%).

Synthesis of triethylcyclohexoxysilane. 11.6 g triethylsilane and a solution of 0.2 g potassium in 20.0 g cyclohexanol were boiled for 2 hours. During this period 2.2 liters hydrogen came off. After distilling off the reaction product from the alkoxide, the product was distilled in a column to give 19.2 g (81.0%) triethylcyclohexoxysilane with b.p. 236.9° (756.0 mm).

Synthesis of triethylbenzyloxysilane. A solution of 0.3 g Na, 14.1 g benzyl alcohol and 11.6 g triethylsilane were heated at the boil for 2 hours; during this period 2.4 liters hydrogen came off. The reaction mixture was distilled at first in vacuum and later in a column. Yield of triethylbenzyloxysilane with b.p. 262.2-263.0° (764.2 mm) was 19 g (80.9%).

Synthesis of triethyl-β-aminoethoxysilane. On heating for an hour 11.6 g triethylsilane with a solution of 0.1 g sodium in 12.2 g ethanolamine, 2.4 liters hydrogen came off. The reaction mixture consisted of two layers (lower one of solution of alkoxide in ethanolamine, upper one of triethyl-β-aminoethoxysilane). Distillation of the upper layer in a column gave 14.9 g (84.9%) triethyl-β-aminoethoxysilane with b.p. 201.7° (761.9 mm).

Synthesis of tri-n-propylisobutoxysilane. To a solution of 0.2 g sodium in 14.8 g isobutyl alcohol was added 15.9 g tri-n-propylsilane. Boiling of the reaction mixture for 11 hours led to evolution of 2.3 liters hydrogen. Two distillations of the reaction mixture in vacuum gave 19.7 g (85.4%) tri-n-propylisobutoxysilane with b.p. 90.5° (5 mm).

Synthesis of tri-n-butyl-tert-butoxysilane. 20.1 g tri-n-butylsilane and a solution of 0.2 g sodium in 14.8 g tert-butyl alcohol were heated in an autoclave at 200-210° for 19 hours. The maximum pressure in the autoclave was 23 atm. During the reaction 2.3 liters hydrogen came off and was collected. After distilling off the excess of alcohol, the reaction mixture was distilled in vacuum to give 10.9 g (80%) tri-n-butyl-tert-butoxysilane with b.p. 120.5° (7 mm).

Synthesis of triethylphenoxysilane. To 18.8 g melted phenol was added 0.1 g aluminum powder and 1.5 g iodine, followed, with stirring, by 11.6 g triethylsilane. Heating of the reaction mixture at the boil for an hour caused 2.5 liters hydrogen to come off. Two distillations of the reaction mixture gave 16.7 g (80.3%) triethylphenoxysilane with b.p. 243.8° (762.8 mm).

Reaction of triethylsilane with sodium methoxide. 2.3 g sodium was dissolved while cooling in 6.4 g methanol. The alcohol was driven off in vacuum in an atmosphere of dry hydrogen, and the residual alkoxide was heated in a hydrogen stream on a water bath for a further 1.5 hours. To the so-prepared sodium methoxide was added 11.6 g triethylsilane. No hydrogen was evolved on boiling this mixture for 3 hours, and all the triethylsilane remained unchanged. A similar result was obtained on prolonged heating of triethylsilane with sodium methoxide in a medium of inert solvent (benzene).

Transesterification of triethylmethoxysilane with butyl alcohols. 14.6 g triethylmethoxysilane, 14.8 g n-butyl alcohol and 0.1 g sodium were slowly distilled in a column. 3.1 g methanol came over at 64.4-66.2° (760.2 mm). Further distillation gave 8.3 g excess n-butyl alcohol with b.p. 115.2-117.3° and 17.0 g triethyl-n-butoxysilane with b.p. 193.0-193.8° (760.2 mm). Yield 90.4% of the theoretical. After redistillation it had:

B.p. 193.8° (760.2 mm), n_D^{20} 1.4210, d_4^{20} 0.8185.

Found %: Si 14.66, 14.70. $C_{10}H_{24}OSi$. Calculated %: Si 14.88.

Transesterification of triethylmethoxysilane with isobutyl alcohol in completely identical conditions gave 14.6 g (77.4%) triethylisobutoxysilane with b.p. 185.9° (755.3 mm).

Found %: Si 14.79, 14.66. $C_{10}H_{24}OSi$. Calculated %: Si 14.88.

Transesterification of triethylmethoxysilane in similar conditions with sec-butyl alcohol leads to formation of only 3-5% triethyl-sec-butoxysilane with b.p. 186-188°, n_D^{20} 1.4203. The greater part of the triethylmethoxysilane remains unchanged.

An attempt to transesterify triethylmethoxysilane with tert-butyl alcohol failed. All the original triethylmethoxysilane was recovered unchanged.

SUMMARY

A study was made of the reaction of n-trialkylsilanes R_3SiH ($R = C_2H_5$, $n-C_3H_7$, $n-C_4H_9$) with alcohols of various structures in presence of alkoxides of lithium, sodium, potassium and rubidium. A dependence was found of the course of this reaction on the structure of the trialkylsilane and alcohol and on the atomic number of the metal in the alkoxide used as catalyst. A mechanism is proposed for the reaction. It is shown that the reaction of trialkylsilanes with alcohols is a simple and convenient method of synthesis of trialkylalkoxysilanes, which are formed in yields of 80-90% of the theoretical. Syntheses were effected of 28 (27 for the first time) trialkylalkoxysilanes, and their physical properties were determined.

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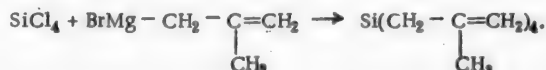
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SYNTHESIS OF TETRAISOBUTYL-, TETRAISOPROPYL-, TETRA-CYCLOHEXYL- AND TETRA- α -NAPHTHTHYLSILANES

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On carrying out the condensation according to the scheme $R_3CX + RMgX \rightarrow R_4C + MgX_2$ at elevated temperature or in presence of $HgCl_2$, Petrov and Chernyshev [1] obtained tetra-n-propyl and tetra-n-butylmethanes in low yields and showed that the synthesis of tetra-n-hexylmethane cannot be realized at all due to the facility of cleavage of HCl from trihexylchloromethane. The synthesis of tetraalkylsilanes, by analogous scheme, takes place with high yields even when using high-molecular alkyl halides [2], both owing to the greater ionization of the $\rightarrow Si - X$ bond and owing to the inability of trialkylhalosilanes to cleave off HX. However, in spite of this, and also of the lower steric hindrance in the synthesis of silanes due to the higher atomic radius of silicon, only triisobutylsilane has been prepared by the action of isobutylsodium on $SiCl_4$ (probably because the fourth atom of chlorine was substituted not by the isobutyl radical but by sodium) [3]. Introduction into the isobutyl radical of a double bond in the beta-position enabled Petrov and Nikishin [4] to overcome the steric hindrances here arising and to obtain tetraisobutenylsilane according to the scheme:



Isopropyl magnesium bromide enters with still greater difficulty into reaction with $SiCl_4$. Only 2 isopropyl radicals could be linked to the silicon atom by means of the organomagnesium synthesis [5, 6]. When using a more active metal (lithium), however, the isopropyl radical takes the place of 3 atoms of chlorine. A fourth isopropyl radical could not be introduced even by the action on triisopropylchlorosilane of a molecule of isopropyllithium.

Similar results were also obtained with the cyclohexyl radical. When utilizing $MgBrC_6H_{11}$ [7] only 2 cyclohexyl radicals can be linked to the silicon atom. When using cyclohexyllithium, its reaction with $SiCl_4$ can give $(C_6H_{11})_3SiCl$. It was impossible, however, to substitute the chlorine atom in $(C_6H_{11})_3SiCl$ by the organomagnesium or organolithium synthesis either with the cyclohexyl radical or with C_2H_5 [8]. The organolithium synthesis also failed to lead to tetra- α -naphthylsilane, tri- α -naphthylsilane being instead formed, according to the scheme [9]:



The same silicohydrocarbon [10] was also obtained according to the scheme:



At the same time tetra- β -naphthylsilane is obtained by analogous schemes in high yields [11].

If $SiCl_4$ is replaced by SiF_4 it is possible even by the organomagnesium synthesis to link 3 isopropyl and cyclohexyl radicals to the silicon atom [12]. By using SiF_4 it is likewise possible to obtain $(\alpha-C_{10}H_7)_3SiF$ according to the scheme [13]:



whereas with $SiCl_4$ only $(\alpha-C_{10}H_7)_2SiCl_2$ is obtained.

Taking into consideration the partial success in overcoming the difficulties by using separately either silane fluorides or organolithium compounds, we decided to make joint use of silane fluoride and organolithium compounds for synthesis of a series of tetrasubstituted silanes containing radicals which cause steric hindrance.

An attempt at the synthesis of tetra- α -naphthylsilane according to the scheme:



was crowned with success.

Since the synthesis was effected at high temperature, the product of synthesis was contaminated by resinous admixtures which could only be removed by chromatography.

As we know, tetracyclohexylmethane could not be obtained either by condensation of tricyclohexylchloro-

methane with cyclohexyl magnesium bromide or by hydrogenation of tetraphenylmethane [14]. On the other hand the synthesis of its silicon analog by the suggested scheme proceeded even after the first step, $\text{SiF}_4 + \text{LiC}_6\text{H}_{11} \rightarrow (\text{C}_6\text{H}_{11})_4\text{Si}$ (8%). Tetracyclohexylsilane was obtained in slightly better yield by a two-step synthesis according to the equation



The fluorine atom in $(\text{C}_6\text{H}_{11})_3\text{SiF}$ could be substituted by the *n*-butyl radical in higher yield (21%).

Synthesis of tetraisobutyl- and tetraisopropylsilanes was effected according to the scheme:



In the table are set forth the properties and yields of the prepared compounds.

Substance	Formula	Boiling or melting point	d_4^{20}	n_D^{20}	Yield (in %)
Tetraisopropylsilane	$\text{C}_{12}\text{H}_{28}\text{Si}$	B.p. 220-228°	0.8006	1.4472	23.8
Tetraisobutylsilane	$\text{C}_{16}\text{H}_{36}\text{Si}$	B.p. 248-250	0.7910	1.4431	63.2
Tetracyclohexylsilane	$\text{C}_{24}\text{H}_{44}\text{Si}$	M.p. 196-198	—	—	11
Tetra- α -naphthylsilane	$\text{C}_{40}\text{H}_{28}\text{Si}$	M.p. 279.6-280	—	—	24.8

The higher reactivity of fluorosilanes, in comparison with chlorosilanes, is evidently explained by the relatively high charge on fluorine and, consequently, the greater ionization of the Si-F bond in comparison with the Si-C bond [15]. The R-Li bond is also more strongly ionized than the R-MgBr bond.

EXPERIMENTAL

Synthesis of tetra- α -naphthylsilane $[(\alpha\text{-C}_{10}\text{H}_7)_4\text{Si}]$. The reaction was carried out in a three-necked, 150 ml flask, fitted with mercury-sealed stirrer, reflux condenser, dropping funnel and gas inlet tube. Naphthyllithium was prepared in the usual way from 30 g (0.14 mole) α -naphthyl bromide and 3 g (0.2 mole) lithium in 50 ml anhydrous ethyl ether. Dropwise addition was made to it of 7 g (0.02 mole) dinaphthylidifluorosilane dissolved in ether. The flask was observed to heat up. After heating the mixture for 2 hours on a water bath, 70 ml kerosene (230-250° fraction) was added, the ether was driven off and the reaction products heated on an oil bath for 25 hours. A grey precipitate came down. After the reaction mixture had been cooled to room temperature, the previously distilled-off ether was added, and decomposition was effected in the usual way.

Brown crystals separated from the ethereal layer and were filtered off. The ethereal layer was dried with calcium chloride. The naphthalene was distilled off with steam. After driving off the ether, crystals came down and were combined with the batch from the ethereal layer. Recrystallization from benzene gave 0.3 g substance with m.p. 224°; this was trinaphthylfluorosilane.

The main bulk of the crystals was insoluble in hot benzene. After 11 recrystallizations from a mixture of ligroine and chloroform, the crystals had a yellow color and melted at 100-110°. The crystals were purified by the chromatographic method. A column 30 cm high and 1.2 cm in diameter was filled with specially prepared Al_2O_3 . The substance was dissolved in a mixture of ligroine (60%) and chloroform (40%), and the solution was run into the column. Elution was effected with the same mixture. 14 fractions were taken off. In fractions 5-10, after evaporating off the solvents, white crystals with m.p. 271-272° came down. After two recrystallizations from a mixture of ligroine and chloroform the crystals had m.p. 279.6-280.1°.

In all 2.9 g (24.6%) tetra- α -naphthylsilane was isolated.

6.59 mg substance: 21.66 mg CO_2 ; 3.19 mg H_2O ; 0.72 mg SiO_2 . 6.25 mg substance: 20.58 mg CO_2 ; 3.12 mg H_2O ; 0.70 mg SiO_2 . Found %: C 89.69, 89.86; H 5.41, 5.58; Si 5.12, 5.24. $\text{C}_{40}\text{H}_{28}\text{Si}$. Calculated %: C 89.51; H 5.26; Si 5.23.

Synthesis of tetraisopropylsilane $(\text{iso-C}_3\text{H}_7)_4\text{Si}$. From 8 g (1 mole) isopropyl chloride and 18 g (2.3 moles) finely flaked lithium in 150 ml anhydrous ethanol in an atmosphere of dry nitrogen was obtained isopropyllithium. To this was added dropwise 36 g (0.2 mole) triisopropylfluorosilane. The reaction mixture was then heated for 26 hours on a water bath. After cooling to room temperature and separating the unreacted lithium, the reaction products were decomposed with water. The ether layer was separated, dried and fractionally distilled to give 9.7 g (23.8%) tetraisopropylsilane with b.p. 220-228°.

Fraction with b.p. 222-224°; n_D^{20} 1.4472; d_4^{20} 0.8006; M_R 66.83, calculated 67.32.

Found %: C 72.60, 72.22; H 13.64, 13.54; Si 13.86, 13.70. $\text{C}_{12}\text{H}_{28}\text{Si}$. Calculated %: C 72.00; H 14.00; Si 14.00.

Synthesis of tricyclohexylbutylsilane (C_6H_{11})₃SiC₄H₉. n-Butyllithium was prepared by the usual method from 30 g butyl bromide (0.22 mole) and 3 g (0.43 mole) finely shredded lithium. To the lithium compound was slowly added 13 g tricyclohexylfluorosilane (0.04 mole) dissolved in anhydrous ethyl ether. The reaction mixture was heated on a water bath for 16 hours; kerosene (200-220° fraction) was then added, the ether was driven off, and the residue was boiled on an oil bath for 5 hours. After cooling to room temperature, the reaction product was decomposed with water. The ether layer was driven off, dried with CaCl₂ and fractionated to give 3.2 g (21.9%) tricyclohexyl-n-butylsilane with b.p. 365-370°, m.p. 133-135°.

Preparation of tetracyclohexylsilane (C_6H_{11})₄Si. Method I. Cyclohexyllithium was prepared in a three-necked, round-bottomed liter flask from 14 g (2 moles) lithium and 100 g (0.89 mole) cyclohexyl chloride in 500 ml anhydrous ethyl ether. To the lithium compound was added dropwise, with stirring, 46 g (0.2 mole) dicyclohexylfluorosilane dissolved in 100 ml anhydrous ethyl ether. The reaction mixture was heated 10 hours on a water bath and then 11 hours on an oil bath with kerosene (190-200° fraction). The previously distilled-off ether was then added, and after working up in the usual manner the product was fractionated in vacuum to give 8.1 g (11.3%) product with m.p. 194°.

Method II. Cyclohexyllithium was prepared by the usual procedure from 100 g (0.89 mole) cyclohexyl chloride and 15 g (1 mole) lithium in a medium of ligroine. SiF₄ was passed into the solution of cyclohexyllithium in ligroine (50-75° fraction) for 4 hours. The contents of the flask were heated for 6 hours on a boiling water bath. Working up in the usual way gave 7.95% yield of tetracyclohexylsilane with m.p. 196-198°.

Found %: Si 7.41, 7.87. C₂₄H₄₄Si. Calculated %: Si 7.77.

Synthesis of tetraisobutylsilane. Isobutyllithium was prepared from 4 g (0.29 mole) lithium and 25 g (0.27 mole) isobutyl chloride in 200 ml anhydrous ethyl ether. To it was slowly added, with stirring, 22 g (0.1 mole) triisobutylfluorosilane. Heat was released. The reaction product was heated 7 hours on a boiling water bath. Decomposition followed by the usual treatment led to separation of 16.3 g (63.2%) tetraisobutylsilane.

B.p. 248-250° (767.6 mm); d_4^{20} 0.7910; n_D^{20} 1.4431; MR_D 85.85, calculated 85.84.

Found %: C 73.7, 73.72; H 13.92; 14.02; Si 11.11, 10.85. C₁₆H₃₆Si. Calculated %: C 75.0; H 14.08; Si 10.92.

SUMMARY

1. It was shown that simultaneous use in the synthesis of tetrasubstituted silanes of RLi (in place of RMgBr) and SiF₄ (in place of SiCl₄) enables the very considerable steric hindrance to be overcome.
2. For the first time were synthesized tetraisopropylsilane, tetraisobutylsilane, tetracyclohexylsilane and tetra- α -naphthylsilane.

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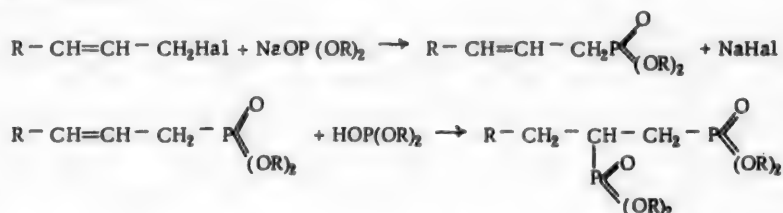
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NEW METHOD OF SYNTHESIS OF ESTERS OF PHOSPHONIC AND THIOPHOSPHONIC ACID

XVIII. ADDITION OF DIALKYLTHIOPHOSPHOROUS ACIDS TO IDENIC DERIVATIVES OF MALONIC AND ACETOACETIC ESTERS

A.N. Pudovik and L.I. Sidnikhina

In connection with a study of allyl rearrangements started in 1946, one of us carried out systematic investigations of reactions of salts of dialkylphosphorous acids with haloallyl derivatives. These investigations led to an interesting and unexpected result. It was found that when the reactions in question were carried out with an equimolar ratio of reactants and in presence of a small amount of a solvent, substitution of the halogen in the haloallyl compound by a phospho group also results in addition of a molecule of dialkyl phosphorous acid at the double bond of the unsaturated phosphonic ester:



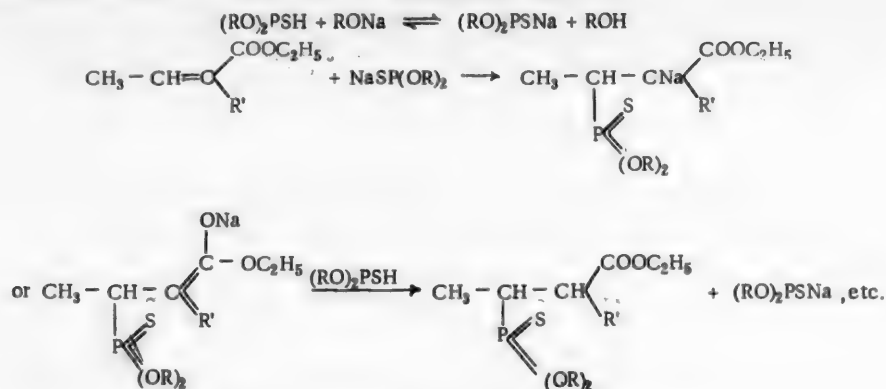
This reaction course was observed in the case of allyl bromide, the isomeric chlorobutenes, methoxychloropentenes and butoxychloropentenes [1]. This observation subsequently formed the basis of a new method of synthesis of esters of phosphonic acids. The essential feature of the method is the addition of dialkyl phosphorous and dialkylthiophosphorous acids, acid esters of alkyl and aryl phosphorous acids, phosphoacetic ester, phosphoacetone, cyanophosphomethane and their monoalkyl derivatives to unsaturated compounds of the electrophilic type. The reaction is carried out in presence of alkoxides of alkali metals. Addition takes place with great facility of the reactants mentioned to esters of unsaturated carboxylic acids - mono- and dibasic - with a double or triple bond. A large number of derivatives of esters of phospho- and thiophosphocarboxylic acids was obtained [2].

In recent years addition reactions have also been effected with unsaturated nitriles [3], ketones [4], aldehydes [5], esters of vinyl alcohols [6], esters of vinylphosphonic acid [7] and anils of various types [8]. With the help of the new method were obtained diverse esters of phospho- and diphosphocarboxylic acids, esters of phosphodicarboxylic and phosphoketocarboxylic acids, cyanophosphonic esters, esters of ketophosphonic acids, unsaturated hydroxyphosphonic esters, esters of phosphoethyl acetate, substituted aminophosphonic esters, various diphosphonoethane derivatives, and thioanalogs of all the foregoing types of compounds. The method is very simple and convenient for preparative purposes, the addition products in the majority of cases being obtained in high yields.

In a paper by one of us the addition was described of dialkylphosphorous acids to ethylidene and benzylidene malonic and ethylidene- and benzylideneacetoacetic esters [9]. It was shown that the reaction proceeds with great facility and that the addition products - esters of dialkylphosphoethyl- and dialkylphosphophenylmethylmalonic and acetoacetic acids - are obtained in yields of 65-85%. In a continuation and broadening of these investigations we decided it would be interesting to study also the addition of dialkylthiophosphorous acids to certain types of idenic derivatives of malonic and acetoacetic esters. As representatives of these acids we chose diethyl- and dibutylthiophosphorous acids. The reaction was effected in presence of sodium ethoxide and butoxide by the usual procedure as described in detail in the above-cited paper [9]. Addition of diethylthiophosphorous and dibutylthiophosphorous acids to ethyldenemalonic and ethylideneacetoacetic ester proceeded very easily and was accompanied by considerable development of heat.

The addition products - ethyl esters of α -(dialkylthiophospho)ethylmalonic and α -(dialkylthiophospho)ethylacetoacetic acids - were obtained in yields of the order of 40-50%, i.e., lower than in the case of dialkylphosphorous acids. The course of the reactions of addition of dialkylthiophosphorous acids to ethyldenemalonic and ethylidene-

acetoacetic esters may be represented by the following general scheme:



where $R = C_2H_5$ and C_4H_9 ; $R' = COOC_2H_5$ and $COCH_3$.

The constants of the compounds prepared are set forth in the table (first four compounds). They are viscous, colorless (in some cases faint-green) liquids with an unpleasant odor.

Preparation No.	Formulas	Boiling point (pressure in mm in parentheses)	n_D^{20}	d_4^{20}	Yield (in %)
1	$CH_3CHCH \begin{array}{l} \nearrow COCH_3 \\ \searrow COOC_2H_5 \end{array}$ $S = P(OC_2H_5)_2$	151-152° (13)	1.4720	1.0919	50
2	$CH_3CHCH \begin{array}{l} \nearrow COCH_3 \\ \searrow COOC_2H_5 \end{array}$ $S = P(OC_4H_9-n)_2$	178-180 (8)	1.4753	1.0710	45
3	$CH_3CHCH(COOC_2H_5)_2$ $S = P(OC_2H_5)_2$	160-161 (3)	1.4655	1.1183	52
4	$CH_3CHCH(COOC_2H_5)_2$ $S = P(OC_4H_9-n)_2$	190-192 (6)	1.4558	1.0616	31
5	$C_6H_5CHCH(COOC_2H_5)_2$ $S = P(OC_2H_5)_2$	210-212 (4)	1.4910	1.1075	51
6	$(CH_3)_2CCH(COOC_2H_5)_2$ $S = P(OC_4H_9-n)_2$	200-202 (4)	1.4679	1.0531	50
7	$(CH_3)_2CCH(COOC_2H_5)_2$ $O = P(OC_2H_5)_2$	170-171 (9)	1.4485	1.1870	41

In presence of sodium alkoxides, dialkylthiophosphorous acids are capable of adding on to benzylidene derivatives of malonic and acetoacetic acids. The product of addition of diethylthiophosphorous acid to the ethyl ester of benzylidenemalonic ester was prepared. It had a high b. p.: (210-212° at 4 mm) and was a very viscous liquid with a faint green color and a weak, unpleasant odor.

Finally we investigated the addition of dibutylthiophosphorous acid and dimethylphosphorous acid to isopropylidenemalonic ester. In the preceding paper [9], in which this problem was also touched upon, it was noted that dialkylphosphorous acids in presence of alkoxides of the alkali metals readily add on to isopropylidenemalonic and isopropylideneacetoacetic esters, but the addition products could not be isolated. In the course of fractionation of the reaction mixture, the

viscosity gradually increased and on further heating it changed into a very viscous, nearly solid polymeric mass.

Our experiments on the addition of dibutylthiophosphorous acid to isopropylidenemalonic ester likewise did not lead to a successful result; in course of fractionation the reaction mass invariably changed into a viscous, resinous mass which decomposed on further heating. Employment of triethylamine as the catalyst likewise did not lead to an addition product; no reaction took place, and the original components were recovered unchanged on distillation. It was observed, however, that addition of sodium butoxide to this distilled mixture of starting components caused the reaction to proceed very smoothly; fractional distillation of the reaction mixture proceeded normally and it was possible to isolate an addition product in satisfactory yield. The application of this somewhat complicated procedure to the reactions of dialkylphosphorous acids with isopropylidene derivatives of malonic and acetoacetic esters, reactions which formerly could not be realized, also had a successful outcome. The product of addition of dimethylphosphorous acid to isopropylidenemalonic ester was obtained - ethyl ester of α -methyl- α -(dimethylphospho)ethylmalonic acid - in a yield of about 50%. The reactions proceed according to the equations:

5 g ethyl isopropylidenemalonate and 5.3 g dibutylthiophosphorous acid was added dropwise a solution of sodium butoxide. Considerable heat was developed by the reaction mixture. After the reaction mixture had been heated on a water bath for 2 hours, the sodium butoxide was neutralized with acetic acid, and the mixture was filtered and distilled. After a small quantity of low-boiling products had come over, the residue quickly thickened and was soon transformed into a resinous mass which decomposed on further heating. Repeated experiments and change of some of the conditions also failed to give satisfactory results.

Experiment 2. The reaction was conducted with the same amounts of reactants but in presence of triethylamine. Addition of the triethylamine was not accompanied by liberation of heat. After 2 hours' heating on a water bath the reaction mixture was fractionated in vacuum. A mixture of the original substances came over. To these was added sodium butoxide in quantity necessary for completion of the reaction. Considerable heat was developed in the reaction mixture during the introduction of the sodium butoxide. The mixture was then worked up as in the previous experiment. Fractionation in vacuum gave 5.1 g ethyl α -methyl- α -(dibutylthiophospho)ethylmalonate with b.p. 200-202° at 4 mm.

Found %: P 7.11. $C_{18}H_{35}O_6PS$. Calculated %: P 7.55.

VII. Addition of dimethylphosphorous acid to ethyl isopropylidenemalonate. Experiment 1. Reactants were 6.5 g ethyl isopropylidenemalonate and 3.5 g dimethylphosphorous acid. The reaction was carried out in presence of sodium methoxide and proceeded with much heat liberation. After heating on a water bath followed by neutralization of the sodium methoxide, the mixture was distilled in vacuum. A small amount of low-boiling materials came over to leave a residue which quickly changed into a thick, resinous mass. Further heating led to decomposition with evolution of a white vapor. A repeat of the experiment under the same conditions was unsuccessful.

Experiment 2. The experiment was carried out with the same amounts of reactants and catalyst, but the reaction mixture was previously heated with triethylamine. By this procedure the fractionation of the reaction mixture proceeded normally. 4.1 g ethyl α -methyl- α -(dimethylphospho)ethylmalonate was isolated with b.p. 170-171° at 9 mm.

Found %: P 9.74. $C_{12}H_{23}O_7P$ Calculated %: P 10.00.

SUMMARY

1. It was shown that dialkylthiophosphorous acids add on to ethylidenemalonic, benzylidenemalonic, isopropylidenemalonic and ethylideneacetoacetic esters.
2. The following addition products were prepared and characterized: ethyl esters of α -(ethylthiophospho)ethylmalonic, α -(dibutylthiophospho)ethylmalonic, α -(diethylphospho)ethylacetoacetic, α -(dibutylthiophospho)ethylacetoacetic, phenyl-(diethylthiophospho)methylmalonic, α -methyl- α -(dimethylphospho)ethylmalonic and α -methyl- α -(dibutylthiophospho)ethylmalonic acids.

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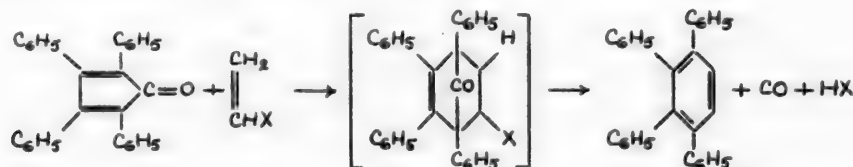
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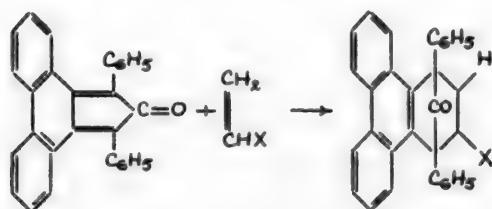
THE ACTION OF SUBSTITUTED VINYL ETHERS AND ESTERS ON CYCLONES

V.S. Abramov and A.P. Pakhomova

Abramov [1] has shown that vinyl ethers and esters can serve as the olefinic component in reactions of diene synthesis with cyclones. The diene synthesis of cyclones with vinyl compounds proceeds with cleavage of the endocarbonyl bridge and removal of alcohol in the case of vinyl ethers, or removal of an acid in the case of vinyl esters, or in general of the molecule HX, where X is any non-carbon atom.



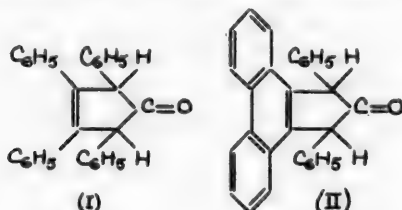
This course of the diene synthesis of vinyl compounds of the type of $\text{CH}_2=\text{CHX}$ is general for cyclones. The behavior of the more reactive phencyclone [2], however, differs from that of all other cyclones. Many dienophiles add on to phencyclone with greater facility than in the case of other cyclones. In reactions of diene synthesis with vinyl compounds, phencyclone gives the normal adducts with an endocarbonyl bridge.



The facility with which phencyclone undergoes addition reactions and the tendency to form stable addition products with an endocarbonyl bridge, in contrast to all other cyclones, must be explained by the specificity of its structure and the specificity of the addition product formed.

Abramov and Shapshinskaya [3] studied the reaction of cyclones with aliphatic and cyclic enol-esters. It was suggested that cyclones and enol esters will react according to the diene synthesis, and since enol esters can be regarded as substituted vinyl esters, then by analogy with vinyl compounds the diene synthesis of cyclones with esters ought to proceed with cleavage of the endocarbonyl bridge and removal of the compound HX.

It was found that in the cases studied, the reactions of cyclone, acencyclone and phencyclone with enol esters do not proceed according to the diene synthesis. Cyclone and phencyclone give products of their reduction: (2,5-dihydrocyclohexadiene) (I) and 2,5-dihydrophencyclone (II).



Reaction of acencyclone with enol esters is accompanied by severe resinification, and it was not possible to isolate any specific substances. The reactions were carried out in a benzene medium.

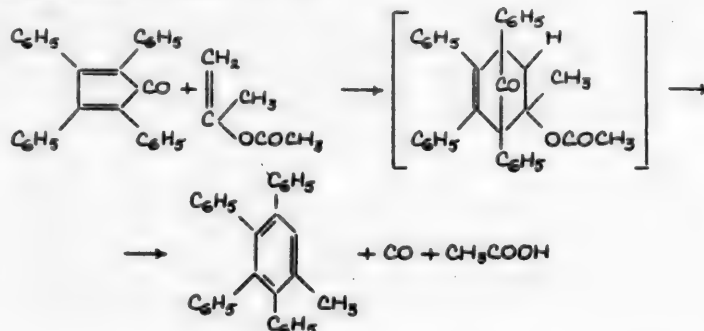
One of us [4] previously obtained dihydrocyclohexadienes by reaction of cyclones with hydrocarbons, alcohols and other organic compounds. Benzene reduces cyclones with great difficulty. In this case we must conclude

that reduction takes place at the expense of enol esters. The mechanism of the reactions taking place was, however, not studied.

In the present research we were interested in a further study of the diene synthesis of cyclones with other

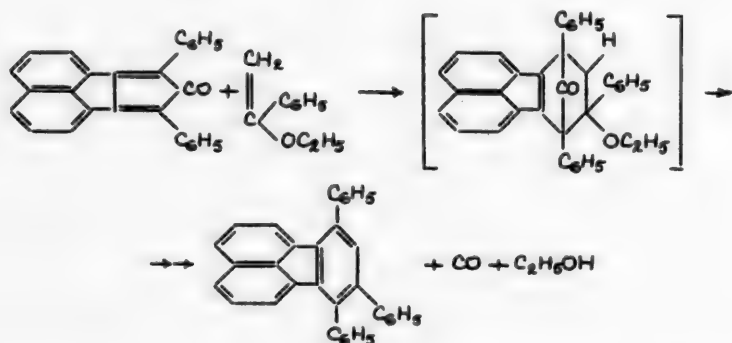
substituted vinyl compounds. We regarded enol esters as β -substituted vinyl ethers which, as was shown, do not react with cyclones according to the diene synthesis. It was necessary to study the behavior in these reactions of α -substituted vinyl esters in order to be able to reach a conclusion about the influence of the position of the substituting group on the diene synthesis of cyclones. We studied the reaction of cyclones with α -substituted vinyl ethers and esters and we established that the α -substituted vinyl ethers and esters, in contrast to the β -substituted ones, undergo the diene synthesis with cyclones.

Cyclone reacts with the α -methylvinyl ester of acetic acid according to the following scheme to give 1-methyl-2,3,4,5-tetraphenylbenzene with m.p. 185-186°:



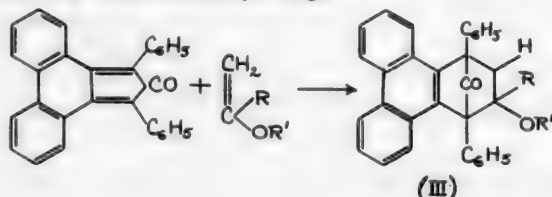
The same product is obtained by the action of α -methylvinyl ethyl ether on cyclone. Reaction of α -phenylvinyl ethyl ether with cyclone gives pentaphenylbenzene [5]. In all cases the endocarbonyl bridge and acid or alcohol are detached during the diene synthesis.

Acceyclone reacts with α -phenylvinyl ethyl ether to give 1,2,5-triphenyl-2,3-(1,8-naphthylene)-benzene with m.p. 193-194° [6]:



Acceyclone reacts with other vinyl ethers with severe resinification and specific reaction products were not isolated.

Phencyclone reacts with α -methylvinyl acetate to give 2,5-endocarbonyl-1-methyl-1-acetoxy-2,5-diphenyl-3,4-(0,0'-biphenylene)- Δ^3 -cyclohexene (III, where $R = CH_3$; $R' = COCH_3$) with m.p. 238-239°; with α -methylvinyl ethyl ether it gives 2,5-endocarbonyl-1-methyl-1-ethoxy-2,5-diphenyl-3,4-(0,0'-biphenylene)- Δ^3 -cyclohexene (III, where $R = C_2H_5$; $R' = C_2H_5$) with m.p. 251-252°, while with α -phenylvinyl ethyl ether it gives 2,5-endocarbonyl-1-ethoxy-1,2,5-triphenyl-3,4-(0,0'-biphenylene)- Δ^3 -cyclohexene (III, where $R = C_6H_5$; $R' = C_2H_5$) with m.p. 269-270°. Phencyclone reacts with α -substituted vinyl ethers and esters according to the diene synthesis and gives normal adducts with retention of the endocarbonyl bridge:



where R is methyl or phenyl, and R' is ethyl or acetyl.

EXPERIMENTAL

Preparation of α -methylvinyl ethyl ether. 15.5 g magnesium turnings was placed in a flask fitted with a mechanical stirrer, a reflux condenser and a dropping funnel; 100 ml dry ether was run in. Into the magnesium was gradually run 92 g methyl iodide. The reaction was completed by heating on a water bath. After the whole of the magnesium had reacted, the reaction mass was cooled to room temperature. With further cooling and stirring, addition was made to the methylmagnesium iodide of 150 g α,β -dibromodiethyl ether dissolved in 100 ml dry ether. During this operation heat was evolved. The course of the reaction was regulated by the speed of addition. After addition was completed, the reaction products were heated on a water bath and then treated with dilute hydrochloric acid. The ether layer was collected and dried, the ether was driven off, and the residue fractionated in vacuum. During fractionation much resinification occurred. A small amount of substance giving a positive reaction for bromine came off.

The distilled product was subjected to cleavage of hydrogen bromide. This was effected with 2% alcoholic solution of KOH with stirring and cooling and with gradual addition of α -methyl bromodiethyl ether. The precipitated potassium bromide was filtered off and the alcoholic solution was carefully fractionated. After three successive fractionations in a Widmer column, the fraction of α -methylvinyl ethyl ether with b.p. 52.5-53.5° and the following constants was collected: n_D^{20} 1.3805, d_4^{20} 0.778, MR 25.68; calculated 26.47.

Reaction of cyclone with isopropenyl acetate. Cyclone was obtained by Dilthey's method [8]. 2 g cyclone, 3 ml isopropenyl acetate and 15 ml dry ether were sealed into a tube. The tube was heated in a furnace at 130-160° for 10 hours and at 180-200° for 23 hours until the crimson color of the solution due to the cyclone had disappeared. Insignificant pressure was detected when the tube was opened. The escaping gases burned with a bluish flame. Benzene was distilled off from the reaction products, and from the residue on cooling were deposited white crystals with m.p. 182-183°, yield 1.9 g (91%). After recrystallization from glacial acetic acid they melted at 185-186°.

0.2004 g substance: 0.6878 g CO₂; 0.118 g H₂O. Found %: C 93.60; H 6.19. C₃₁H₂₄. Calculated %: C 93.94; H 6.06.

Reaction of cyclone with α -methylvinyl ethyl ether. 2 g cyclone, 1.5 ml α -methylvinyl ethyl ether and 15 ml benzene were sealed into a tube under carbon dioxide. The tube was heated at 180-200° for 75 hours. Insignificant pressure was detected when the tube was opened. The benzene was distilled off, and the resinous residue solidified when anhydrous ethanol was added. After washing with ethanol the residue had m.p. 180-185°, yield 1.1 g (50%). After recrystallization from glacial acetic acid the substance melted at 185-186°. A mixed test with the product of reaction of cyclone with isopropenyl acetate melted at 185-186°.

Reaction of cyclone with α -phenylvinyl ethyl ether. 2 g cyclone, 3 ml α -phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube at 120-150° for 5 hours and at 180-200° for 62 hours. The contents of the tube had a brown color. Slight pressure was detected on opening the tube. The benzene was distilled off from the reaction products. On cooling, the residue deposited white crystals which were filtered and washed with anhydrous ethanol; m.p. 237-240°, yield 0.7 g (29%). After recrystallization from a 1:1 mixture of benzene and ethanol the m.p. was 242-243°. Pentaphenylbenzene has m.p. 245-246° [8].

Reaction of acetylcyclone [9] with α -phenylvinyl ethyl ether. 2 g acetylcyclone, 3 ml α -phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube in a furnace at 120-150° for 5 hours and at 180-200° for 24 hours. The finish of the reaction was marked by decolorization and by development of a brown color of the solution. Slight pressure was detected when the tube was opened. The benzene was driven off and the residue deposited yellowish crystals, weight 1.8 g (78%), m.p. 182-186°. After recrystallization from benzene-ethanol they melted at 193-194°. 1,4,5-Triphenyl-2,3-(1,8-naphthylene)benzene has m.p. 195-196° [6].

Reaction of acetylcyclone with isopropenyl acetate. 2 g acetylcyclone, 3 ml isopropenyl acetate and 15 ml benzene were heated in a sealed tube at 180-200° for 30 hours. The close of the reaction was indicated by decolorization and formation of a light brown color in the solution. After opening the tube and driving off the benzene, crystallization of the residue only commenced after two weeks. Regularly formed crystals were not obtained and the melting point was indefinite.

Reaction of phencyclone [9] with isopropenyl acetate. 2 g phencyclone, 1.5 ml isopropenyl acetate and 15 ml benzene were heated in a sealed tube on a boiling water bath for 35 hours. The termination of the reaction was marked by disappearance of the green color of the phencyclone solution. The tube was opened and the benzene was driven off. On cooling, the residue deposited white crystals weighing 2.2 g (91%) and melting at 235-238°. After

recrystallization from a mixture (1:1) of alcohol and benzene, they melted at 238-239°.

0.1848 g substance: 0.5726 g CO₂; 0.0900 g H₂O. Found %: C 84.50; H 5.41. C₃₄H₂₈O₃. Calculated %: C 84.64; H 5.39.

Reaction of phencyclone with α -phenylvinyl ethyl ether. 2 g phencyclone, 3 ml α -phenylvinyl ethyl ether and 15 ml benzene were heated in a sealed tube in a furnace at 120-150° for 5 hours. The end of the reaction was marked by disappearance of the green color of the solution. The tube was opened and the benzene was driven off. The residue crystallized after cooling and addition of glacial acetic acid. The filtered product, after washing with ethanol, had m.p. 215-225°, yield 0.9 g (35%). After several recrystallizations from glacial acetic acid it had m.p. 269-270°.

0.1822 g substance: 0.5888 g CO₂; 0.0944 g H₂O. Found %: C 88.13; H 5.75. C₃₉H₃₀O₂. Calculated %: C 88.30; H 5.66.

Reaction of phencyclone with α -methylvinyl ethyl ether. 2 g phencyclone, 1.5 ml α -methylvinyl ethyl ether and 15 ml benzene were sealed into a tube under carbon dioxide. The tube was heated in a boiling water bath for 34 hours. The end of the reaction was indicated by disappearance of the green color of the solution, which changed to straw-yellow. Cooling of the tube resulted in separation of faint-yellow crystals. The tube was opened and the crystals were filtered and washed with benzene and ethanol; m.p. 200-210°; yield 0.8 g (35%); after recrystallization from a mixture of ethanol and benzene the m.p. was 251-252°.

0.1222 g substance: 0.3900 g CO₂; 0.0675 g H₂O. Found %: C 87.04; H 6.14. C₃₄H₂₈O₃. Calculated %: C 87.18; H 5.98.

SUMMARY

1. It was established that cyclones react with α -substituted vinyl ethers and esters by the diene synthesis, in contrast to β -substituted ethers or esters.
2. Cyclone and acecyclone react with α -substituted vinyl ethers and esters by the diene synthesis which proceeds with rupture of the endocarbonyl bridge and removal of alcohol (in the case of vinyl ethers) or of acid (in the case of vinyl esters).
3. Phencyclone reacts with vinyl ethers and esters by the diene synthesis with formation of addition products with an endocarbonyl bridge.

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Received February 6, 1954

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* T.p. = C.B. Translation pagination.

ACTION OF HYDROGEN SULFIDE ON ESTERS OF ARSENOUS ACID

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As we know, on passing hydrogen sulfide through a solution of arsine oxides with heating, the oxygen can be replaced by sulfur to give the corresponding arsine sulfides:



Compounds so prepared were phenarsazine sulfide [1], phenylarsine sulfide [2], etc.

In this investigation we studied the action of hydrogen sulfide on esters of arsenous acid, a problem of some theoretical interest since, if the reaction



could be realized, this route could lead relatively simply to esters of thioarsenous acid, compounds which have hardly been investigated.

However, on passing dry hydrogen sulfide into a solution of an ester of arsenous acid in dry toluene or anhydrous diethyl ether, a yellow precipitate of arsenic sulfide came down according to the equation:



The reaction took place with liberation of heat. Consequently the action of hydrogen sulfide on esters of arsenous acid is completely analogous to the action of water: esters of arsenous acid are easily decomposed by hydrogen sulfide with formation of the corresponding alcohol and arsenic sulfide. Arsenic sulfide comes down quantitatively, and this suggests the possibility of utilization of this reaction for analysis of the respective organic derivatives of arsenic.

EXPERIMENTAL

The esters of arsenous acid used in our work were prepared by reaction of the corresponding alcohol with arsenic trichloride in presence of pyridine in a medium of diethyl ether. The physico-chemical constants of the prepared esters were in good agreement with the constants reported in the literature.

Action of hydrogen sulfide on tri-n-octyl arsenite. Hydrogen sulfide, previously dried by passage through three U-tubes with phosphorus pentoxide and glass wool, was passed through a solution of 6.26 g tri-n-octyl arsenite in 50 ml anhydrous diethyl ether in a round-bottomed flask fitted with a reflux condenser. Arsenic trisulfide soon came down and slight heating was observed. After passage of the hydrogen sulfide had been stopped, the precipitate of arsenic trisulfide was filtered, washed with dry ether and dried for several hours in a drying cupboard at 130°. Weight of precipitate after drying, 1.7 g (the theoretical requirement was 1.67 g).

Found %: As 60.6, As_2S_3 . Calculated %: As 60.9.

The filtrate was transferred to an Arbuzov flask. The ether was driven off and the residue distilled in vacuum, when the whole residue (4.1 g) of n-octyl alcohol came over at 90° (13 mm); d_4^{20} 0.8269, n_D^{20} 1.4288.

Action of hydrogen sulfide on ethyl, isopropyl and isobutyl esters of arsenous acid. Treatment with hydrogen sulfide of solutions of triethyl arsenite, triisopropyl arsenite and triisobutyl arsenite in toluene in the above apparatus led to rapid separation of arsenic trisulfide and slight development of heat. The weight of the residue of arsenic trisulfide after drying in all cases was slightly higher than the theoretical requirement.

SUMMARY

It was established that esters of arsenous acid are decomposed with facility by hydrogen sulfide, with separation of arsenic trisulfide and the corresponding alcohol.

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Received January 12, 1954

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SYNTHESIS OF SOME DERIVATIVES OF ALIPHATIC β -AMINO ACIDS

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The preparation of aromatic hydroxamic acids has been adequately described in the literature [1], whereas relatively little has been published about aliphatic hydroxamic acids. Information is completely lacking about hydroxyamic acids which are derivatives of compounds with mixed functions. It was therefore a matter of interest to prepare hydroxamic acids which are derivatives of some aliphatic β -amino acids.

β -Aminodecanoic (β -aminocapric), β -aminoundecanoic and β -aminolauric acids were obtained by the method of Rodionov and Zvorykina by condensation of the corresponding aldehydes with malonic acid in presence of alcoholic ammonia [2, 3]. The ethyl esters were prepared from these acids by the usual method. Reaction of an aqueous alkaline solution of hydroxylamine with the esters of β -amino acids in presence of aqueous KOH gave the β -amino-alkylhydroxamic acids.

In the literature is reported the isolation of hydroxamic acids of the aliphatic series with the help of copper acetate followed by decomposition of the copper salt with hydrogen sulfide [4]. We isolated β -aminodecanoic, β -aminoundecanoic and β -aminolauric hydroxamic acids in the form of the hydrochlorides, as was described in the case of hydroxamic acids of acids of the aromatic series [5].

EXPERIMENTAL

β -Aminoundecanoic acid. A mixture of 10 g nonanal 7:35 g malonic acid and 22 ml 5.48% alcoholic ammonia (1.218 g NH_3) was heated until carbon dioxide ceased to come off. The reaction mass was worked up with 150 ml warm water. On standing, the aqueous layer deposited white crystals which after three recrystallizations from alcohol had m.p. 196-197° with decomposition. Weight 1.0 g. The compound was soluble in hot water, alcohol, hydrochloric acid and sodium bicarbonate, insoluble in ether or acetone.

8.482 mg substance: 0.518 mg N_2 (22°, 740 mm). Found %: N 6.82. $\text{C}_{11}\text{H}_{23}\text{O}_2\text{N}$. Calculated %: N 6.96.

β -Aminolauric acid was prepared by the method described for β -aminoundecanoic acid. From 10 g capric aldehyde, 6.7 g malonic acid and 10 ml 11% alcoholic ammonia solution (1.12 g NH_3) was obtained 1.3 g β -aminolauric acid. After crystallization from alcohol it had m.p. 194-195°.

7.96 mg substance: 0.471 mg N_2 (19°, 741 mm). Found %: N 6.74. $\text{C}_{12}\text{H}_{25}\text{O}_2\text{N}$. Calculated %: N 6.51.

Ethyl β -aminodecanoate. A solution of 4 g β -aminodecanoic acid [2] in 20 ml anhydrous ethanol was saturated with hydrogen chloride until the acid had dissolved completely. The reaction mixture was heated for an hour on a water bath, after which the excess ethanol was distilled off. To the residue was added an equal volume of water (1.5-2 ml) and 10 ml ether, and the mixture shaken with intense cooling with a slight excess of 33% sodium hydroxide solution. After separation of the ethereal layer the aqueous layer was salted out with potassium carbonate and again extracted with ether. After drying the ethereal solution and removal of the solvent, the residue was thrice distilled in vacuum. The ethyl ester of β -aminodecanoic acid is an oily, viscous liquid with b.p. 151-153° at 20 mm. Weight 2.9 g.

5.152 mg substance: 12.45 mg CO_2 ; 5.171 mg H_2O . Found %: C 65.95; H 11.23. $\text{C}_{13}\text{H}_{25}\text{O}_2\text{N}$. Calculated %: 66.91; H 11.7.

Ethyl β -aminoundecanoate was prepared by the same method. From 6 g β -aminoundecanoic acid was obtained 4.8 g of the ethyl ester. After three distillations it had b.p. 164-167° at 20 mm.

4.289 mg substance: 10.612 mg CO_2 ; 4.459 mg H_2O . Found %: C 67.52; H 11.63. $\text{C}_{13}\text{H}_{27}\text{O}_2\text{N}$. Calculated %: C 68.05; H 11.87.

Ethyl β -aminolaurate was prepared by the same procedure. From 6.6 g β -aminolauric acid was obtained 4.9 g of ethyl β -aminolaurate. After three distillations it had b.p. 168-173° at 20 mm.

3.846 mg substance: 9.730 mg CO_2 ; 3.963 mg H_2O . Found %: C 69.04; H 11.53. $\text{C}_{14}\text{H}_{29}\text{O}_2\text{N}$. Calculated %: C 69.07; H 12.01.

β -Aminodecanehydroxamic acid hydrochloride. To a 40% aqueous solution of 0.52 g potassium hydroxide was added 0.65 g hydroxylamine hydrochloride. The precipitate of potassium chloride was separated and to the

filtrate was added 1 g ethyl β -aminodecanoate and a further 0.52 g potassium hydroxide in the form of a 40% aqueous solution. The mixture was vigorously shaken until a homogeneous solution was obtained. The solution was acidified with 10% hydrochloric acid until weakly acid to congo. After addition of 30 ml anhydrous ethanol and separation of the potassium chloride, the solution was concentrated in vacuum. The residue in the form of an oily liquid was dried over phosphorus pentoxide and crystallized from dry acetone. Yield 0.5 g β -Aminoundecanehydroxamic acid hydrochloride forms white crystals with m. p. 112°, highly soluble in alcohol, water, and hot benzene; insoluble in chloroform and ether. It gives a violet color with iron chloride.

6.325 mg substance: 0.658 N_2 (20°, 723 mm). Found %: N 11.52. $C_{10}H_{23}O_2N_2Cl$. Calculated %: N 11.70.

β -Aminoundecanehydroxamic acid hydrochloride was prepared by the same method. From 1 g ethyl β -aminoundecanoate and 0.6 g hydroxylamine hydrochloride in aqueous alkali solution (0.49 g KOH) was obtained 0.4 g β -aminoundecanehydroxamic acid hydrochloride. After crystallization from acetone it had m. p. 119-120° with decomposition.

4.146 mg substance: 0.394 ml N_2 (19°, 727 mm). Found %: N 10.69. $C_{11}H_{25}O_2N_2Cl$. Calculated %: N 11.08.

β -Aminolaurichydroxamic acid hydrochloride was prepared by the same method. From 1 g ethyl β -aminolaurate in aqueous alkali solution (0.46 g KOH) and 0.57 g hydroxylamine hydrochloride in aqueous alkali solution (0.46 g KOH) was obtained 0.5 g β -aminolaurichydroxamic acid with m. p. 118° (with decomposition) after crystallization from acetone.

6.507 mg substance: 0.618 ml N_2 (29.5°, 731 mm). Found %: N 10.31. $C_{12}H_{27}O_2N_2Cl$. Calculated %: N 10.49.

SUMMARY

1. Reaction of aldehydes with malonic acid and alcoholic ammonia by the method of Rodionov and Zvorykina gave β -aminoundecanoic and β -aminolauric acids.

2. The ethyl esters and the corresponding hydroxamic acids were prepared from the above β -amino acids and also from β -aminocaproic acid.

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Received January 29, 1954

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* T. p. = C. B. Translation pagination.

THE REACTION OF METHYL ACRYLATE WITH ORGANOMAGNESIUM COMPOUNDS

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In the preceding communication [1] it was shown that reaction of isopropyl magnesium bromide with methyl methacrylate gives, instead of diisopropyl isopropenyl carbinol, mainly the dimethyl ester of α, α' -dimethyl- α -isobutylglutaric acid. In the present research we investigated the possibility of formation of vinyl alcohols by the reaction of methyl acrylate with isopropyl magnesium bromide and ethyl magnesium bromide.

Reaction of isopropyl magnesium bromide with methyl acrylate gave two main products: a liquid boiling at 98-99° (2 mm) and a crystalline substance with m.p. 167.5-168°. The liquid product did not contain active hydrogen, did not react with semicarbazone acetate, and did not give a qualitative reaction for the double bond. Determination of the elementary composition, molecular weight and molecular refraction showed that the liquid product was dimethyl α -isobutylglutarate in an insufficiently pure form. It could not be purified by distillation. Hydrolysis of the ester with aqueous potassium carbonate solution gave a crystalline acid whose analytical data and melting point identified it as the α -isobutylglutaric acid prepared for the first time by Rydon [2].

The crystalline product with m.p. 167.5-168° did not react with methyl magnesium iodide or with reagents for the carbonyl group, and did not give a qualitative reaction for the double bond. The percent content of carbon and hydrogen corresponded to the general formula $C_{18}H_{30}O_3$. The neutralization equivalent was 296.6. The compound did not dissolve in benzene, glacial acetic acid, dioxane or water.

The percent content of carbon, hydrogen and silver in the silver salt corresponded to the formula $C_{18}H_{29}O_3Ag \cdot H_2O$.

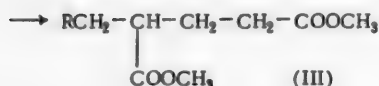
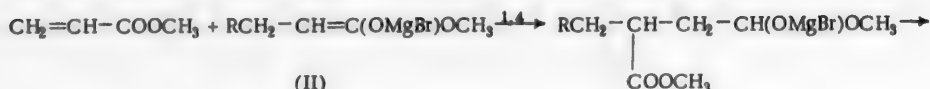
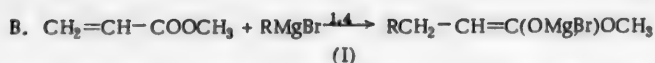
Ultraviolet analysis of the alcoholic solution of the compound $C_{18}H_{30}O_3$ revealed a sharp maximum of absorption at 2940 Å. From the paper of Temkin and Tikhomolova [3] we know that such a maximum is characteristic of ketones possessing substituents in the α -position to the carbonyl group, for example diisopropyl ketone. On boiling, the crystalline compound with aqueous permanganate solution, rapid decolorization took place with formation of isovaleric and oxalic acids. On the basis of the foregoing observations, we may suggest that the crystalline product is 1,3,5-triisobutylcyclohexane-2,4,6-trione. A similar type of compound has been previously prepared. Thus, Combes [4, 5] heated butyryl chloride with $AlCl_3$ and obtained a compound with the formula $C_{12}H_{18}O_3$ to which he attributed the structure of triethylcyclohexanetrione. On hydrolysis of this compound with 25% KOH solution butyric acid and butyric acid were obtained. On carrying out the hydrolysis of triisobutylcyclohexanetrione under similar conditions we isolated diisoamyl ketone (isocaproic) and isocaproic acid. Consequently, the reaction of isopropyl magnesium bromide with methyl acrylate does not lead to appreciable amounts of the tertiary alcohol, diisopropylvinyl carbinol.

Petrov and Radzhabova [6] also point out that the action of isopropyl magnesium bromide on methyl acrylate cannot lead to a tertiary alcohol; in the subsequent experiments, therefore, we used ethyl magnesium bromide in place of isopropyl magnesium bromide. But even in this case diethylvinyl carbinol could not be isolated in the pure form.

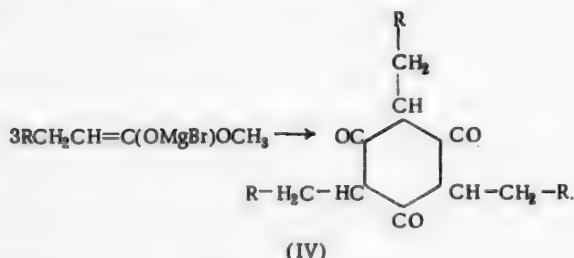
From the mixture remaining after distilling off the ester were isolated two main products: one with b.p. 184-186° and the other with b.p. 108-109° (6 mm). The first product proved to be dibutyl ketone, and the second dimethyl α -n-propylglutarate. Hydrolysis of the ester gave α -n-propylglutaric acid. Attempts to isolate in the pure form 1,3,5-tri-n-propylcyclohexane-2,4,6-trione did not meet with success. In all cases the decomposition of the organomagnesium complex and formation of the high-boiling fractions under the most diverse conditions gave, in place of tripropyltricyclohexanetrione, products of hydrolysis of the latter - dibutyl ketone and valeric acid.

On the basis of the foregoing observations, the following general scheme for the reaction of alkyl magnesium bromides with methyl acrylate may be proposed:

A. Usual reaction of formation of tertiary alcohols.



C.



Reaction course A is not exclusively possible. During the course of the reaction in direction B, addition of the alkyl magnesium bromide to methyl acrylate takes place in the 1,4-position with formation of the magnesium bromide enolate of the ester of the monobasic acid (I), which reacts with a second molecule of methyl acrylate like a true organomagnesium compound of the type of RMgBr , with formation of the magnesium bromide enolate of the ester of the dibasic acid (II); decomposition of the latter with water gives the dimethyl ester of the substituted glutaric acid (III), hydrolysis of which leads to the substituted glutaric acid.

Evidently there is also a third reaction course C in which three molecules of (I) condense with formation of a partial ketal, a substituted cyclohexanetrione thermal decomposition or hydrolysis in mild conditions of which gives the substituted cyclohexanetrione (IV). We succeeded in isolating and completely characterizing this cyclohexanetrione with $\text{R} = \text{iso-C}_3\text{H}_7$; with $\text{R} = \text{C}_2\text{H}_5$ we isolated the products of its hydrolysis — dibutyl ketone and valeric acid.

Addition of alkyl magnesium halides to unsaturated ketones and to unsaturated esters in the 1,4-position was first reported by Kohler [7]. On the other hand, it was also established that reaction of certain ketones with organomagnesium compounds does not result in addition at the carbonyl group but in enolization of the latter [8], the enolate formed behaving like a true Grignard reagent of the type of RMgX [9]. We know from the work of Kabachnik and Mastyukova [10] that magnesium enolates, incapable of changing into compounds of the RMgX type, can under many conditions, for example on methoxymethylation, also form O- and C-derivatives. According to Nesmeyanov [11] the explanation of this formation of two series of derivatives (in the absence of tautomerism) must be sought in the susceptibility of molecules containing conjugated bonds to "rearrangement of the reaction center" in the instant of reaction under the influence of the attacking reactant and under specific conditions of the reaction medium.

The successive occurrence of two reactions: 1) addition of alkyl magnesium bromide to methyl acrylate in the 1,4-position with formation of (I); and 2) reaction of (I) like a compound of the RMgX type with a second molecule of methyl acrylate, may lead in the case which we have investigated to formation of esters of substituted glutaric acids (III).

EXPERIMENTAL

Action of isopropyl magnesium bromide on methyl acrylate

To an ethereal solution of isopropyl magnesium bromide, prepared from 6 g magnesium and 31 g isopropyl bromide in 150 ml ether, was added at 0° 11 g methyl acrylate in 150 ml ether. The organomagnesium complex was decomposed with ice-water. The ether layer was decanted. The residue was treated with dilute hydrochloric acid, then with ether. The ether extract was washed with sodium carbonate and with water and added to the main ethereal solution and dried with Na_2SO_4 . The liquid (17.7 g) remaining after driving off the ether boiled in the range of $25-150^\circ$ (3 mm). Further temperature rise led to separation in the distillation flask of a crystalline material (2.0 g). Fractionation of the liquid in a column gave a fraction (11.0 g) with b.p. $98-99^\circ$ (2 mm):

n_D^{20} 1.4338, d_4^{20} 0.9759.

0.4275 g substance; 11.89 g benzene; Δt 0.880° . Found %: M 211.1. $\text{C}_{11}\text{H}_{20}\text{O}_4$. Calculated: M 216.3.

A mixture of 11 g of the substance, 200 ml water and 20 g potassium carbonate was boiled for 16 hours. To the solution, with cooling and stirring, was added 24 ml H_2SO_4 (1 : 3). The precipitated solid acid was extracted with ether to give 6.2 g crystals with m.p. 67.5–68° (from a mixture of ligroine and acetone).

0.0948 g sub.: 0.1984 g CO_2 ; 0.0748 g H_2O . 0.2387 g sub.: 10.00 g acetic acid: Δt 0.250°. 0.1036 g sub.: 11.7 ml NaOH (T 0.003764). Found %: C 57.11; H 8.82; M 186.1; neut. equiv. 94.12. $\text{C}_9\text{H}_{16}\text{O}_4$. Calculated %: C 57.40; H 8.58; M 188.2; neut. equiv. 94.11.

0.1676 g sub.: 0.1612 g CO_2 ; 0.0557 g H_2O ; 0.0866 g Ag. Found %: C 25.48; H 3.87; Ag 51.54. $\text{C}_9\text{H}_{14}\text{O}_4\text{Ag}_2 \cdot \text{H}_2\text{O}$. Calculated %: C 25.75; H 3.87; Ag 51.39.

The analytical data agreed with the formula of α -isobutylglutaric acid [2]. The silver salt comes down with one molecule of water of crystallization.

Examination of the crystalline residue in the distillation flask. The residue which came down in the flask with resin was separated on a porous plate in the form of white lustrous crystals with m.p. 167.5–168° (from dilute alcohol or acetone).

0.0892 g sub.: 0.2393 g CO_2 ; 0.0844 g H_2O . 0.2363 g sub.: 8.4 ml KOH (in alcohol, T 0.005321). Found %: C 73.21; H 10.59; neut. equiv. 296.6. $\text{C}_{18}\text{H}_{30}\text{O}_3$. Calculated %: C 73.43; H 10.29; neut. equiv. 294.5. 0.1261 g sub.: 0.2358 g CO_2 ; 0.0017 g H_2O ; 0.0329 g Ag. Found %: C 51.14; H 7.26; Ag 26.09. $\text{C}_{18}\text{H}_{29}\text{O}_3\text{Ag} \cdot \text{H}_2\text{O}$. Calculated %: C 51.57; H 7.46; Ag 25.72.

Analysis of the alcoholic solution (concentration 0.0002 M) in a SF-11 spectrophotometer gave an absorption maximum at 2940 Å (optical density of solution 1.25).

Oxidation of product with m.p. 167.5–168°. A mixture of 4 g compound and 400 ml 1% KMnO_4 solution was put into a three-necked flask fitted with stirrer, reflux condenser and thermometer. The solution was decolorized by boiling for 0.5 hour. The MnO_2 was filtered off, washed with hot water and extracted with ether. From the ethereal extract was obtained 1.3 g original substance with m.p. 166–167°. No neutral products were detected in the aqueous filtrate. Four fractions of volatile acids (0.8 g) were obtained and analyzed in the form of silver salts.

1st fraction, 0.1868 g sub.: 0.0864 g Ag; Ag %: 51.62; 4th fraction, 0.496 g sub.: 0.253 g Ag; Ag % 51.00. The 2nd and 3rd fractions had intermediate contents of silver. $\text{C}_8\text{H}_9\text{O}_2\text{Ag}$. Calculated %: Ag 51.62.

From the residue of the salts was obtained an anilide with m.p. 103–105°. The data agree with the formula of isovaleric acid. After driving off the volatile acids, the solution was extracted with ether in a Soxhlet to give 0.3 g oxalic acid with m.p. 187–188°.

Hydrolysis of product with m.p. 167.5–168°. A mixture of 4 g substance, 10 g KOH and 30 ml water was boiled under reflux for 8 hours. The neutral products were distilled with steam and the distillate extracted with ether. Removal of the ether left 2 g substance distilling at 83–84° (4–5 mm):

n_D^{20} 1.4259, d_4^{20} 0.8210, M_R 53.14. $\text{C}_{11}\text{H}_{22}\text{O}$. Calculated 53.01.

The data agreed with diisoamyl ketone (isocaprone). A semicarbazone does not come down. Analysis of the alcoholic solution (concentration 0.348 M) in the SF-11 spectrophotometer revealed an absorption maximum at 2800 Å (optical density of solution 1.07), indicating the presence of a carbonyl group in the compound).

After distilling off the neutral products, the solution was acidified with the calculated amount of H_2SO_4 , and the volatile acids were distilled off (0.75 g) and converted to their silver salts:

0.2431 g sub.: 0.1180 g Ag. Found %: Ag 48.54. $\text{C}_8\text{H}_{11}\text{O}_2\text{Ag}$. Calculated %: Ag 48.38.

The data agreed with those for isocaproic acid. The solution remaining after distillation of the volatile acids was extracted with ether in a Soxhlet to give 1.1 g of original substance with m.p. 163–165°.

The foregoing experiments lead to the conclusion that the compound with m.p. 167.5–168° is 1,3,5-triisobutylcyclohexane-2,4,6-trione.

Action of ethyl magnesium bromide on methyl acrylate

The organomagnesium synthesis was conducted as before using 12 g Mg, 54 g ethyl bromide and 22 g methyl acrylate in the appropriate amount of ether. Removal of the ether left 30 g product distilling at 50° (30 mm) – 120° (8 mm). In the trap was found 2 g methyl acrylate. Repeated distillation gave three fractions: 1st 130–135° 2.9 g; 2nd 184–186°, 5.0 g; 3rd 108–109° (6 mm), 6.4 g. Resin (in flask) 11 g.

Analysis of 1st fraction: 0.0720 g sub.: 9.9 ml CH_4 (15°, 761 mm). Found %: active H 0.65, $\text{C}_7\text{H}_{14}\text{O}$. Calculated %: active H 1.00.

The fraction is impure diethylvinyl carbinol.

Analysis of 2nd fraction: n_D^{20} 1.4205, d_4^{20} 0.8281, MR_D 43.52, $\text{C}_9\text{H}_{18}\text{O}$. Calculated 43.77.

The substance forms a semicarbazone with m.p. 88–89° (from dilute alcohol).

0.0709 g sub.: 12.6 ml N_2 (18°, 779.1 mm). Found %: N 21.10, $\text{C}_{10}\text{H}_{21}\text{ON}_3$. Calculated %: N 21.02.

The data correspond to dibutyl ketone [12].

Hydrolysis of 3rd fraction. A mixture of 11 g substance, 10 g KOH and 50 ml alcohol was boiled for 6 hours. After dilution with water and evaporation of the alcohol, the product was acidified with the calculated amount of H_2SO_4 to give 5.1 g acid with m.p. 68–69° (from water).

0.1722 g sub.: 20.4 ml NaOH (T 0.003875). Found: Neut. equiv. 87.14, $\text{C}_8\text{H}_{14}\text{O}_4$. Calculated neut. equiv. 87.10. 0.2139 g sub.: 0.1186 g Ag. Found %: Ag 55.44, $\text{C}_8\text{H}_{12}\text{O}_4\text{Ag}_2$. Calculated %: Ag 55.68.

The data correspond to α -n-propylglutaric acid [13]. The residue in the flask did not crystallize.

Hydrolysis of residue. A mixture of 11 g resin, 10 g KOH and 150 ml dilute alcohol (1:1) was boiled for 6 hours. From the neutral products was isolated 1.3 g substance boiling at 184–186°. The semicarbazone had m.p. 88–89°. The data corresponded to dibutyl ketone. A silver salt was prepared from the volatile acids which distilled with steam.

0.1930 g sub.: 0.0982 g Ag. Found %: Ag 50.88, $\text{C}_5\text{H}_9\text{O}_2\text{Ag}$. Calculated %: Ag 51.62.

The anilide had m.p. 59–61°. The data corresponded to valeric acid. Decomposition of the organomagnesium complex with saturated NH_4Cl solution gave the same results.

SUMMARY

1. The reactions of methyl acrylate with ethyl magnesium bromide and isopropyl magnesium bromide were studied.
2. It was shown that the reaction proceeds simultaneously in several directions. There are formed, together with a small amount of tertiary olefinic alcohols, dimethyl esters of α -substituted glutaric acids – dimethyl α -propylglutarate and dimethyl α -isobutylglutarate, which on hydrolysis give α -propylglutaric and α -isobutylglutaric acid.
3. Formation of dimethyl esters of α -substituted glutaric acids can be attributed to the addition of alkyl magnesium bromide to methyl acrylate in the 1,4-position with formation of the enolate of the ester of a monobasic acid, and to the subsequent addition of the resultant enolate, in the form of a compound of the RMgBr type, to a second molecule of methyl acrylate, again in the 1,4-position, with formation of the enolate of the ester of a dibasic acid.
4. Condensation of three molecules of ester enolate gives partial ketals of substituted derivatives of cyclohexanetrione which, on thermal decomposition or hydrolysis, give substituted derivatives of cyclohexanetrione.
5. 1, 3, 5-Trisubstituted cyclohexane-2,4,6-trione was isolated and characterized. Instead of 1,3,5-tri-n-propylcyclohexane-2,4,6-trione, the products of its hydrolysis – dibutyl ketone and valeric acid – were isolated.

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Received March 2, 1954

Leningrad State University

* T. p. = C. B. Translation pagination.

OXIDATION OF VINYLACETYLENIC HYDROCARBONS WITH ORGANIC HYDROPEROXIDES

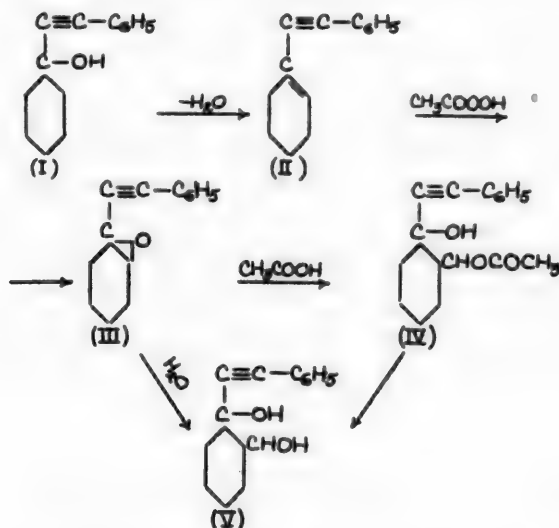
II. OXIDATION OF 1-PHENYLETHINYLCYCLOHEXENE-1 WITH ACETYL HYDROPEROXIDE

N. M. Malenok and S. D. Kulkina

Several authors have studied the chemical transformations of oxides of cyclopentene [1], cyclohexene [2] and oxides of cyclohexenes containing various hydrocarbon radicals: methyl [3], phenyl [4], methylphenyl [5], etc.

In the present research we studied the oxide of 1-phenylethynylcyclohexene-1 (III). It was synthesized by Iotsich's method: phenylacetylene and cyclohexanone gave the alcohol, 1-phenylethynylcyclohexan-1-ol(I), which was dehydrated with potassium bisulfate to the unsaturated hydrocarbon, 1-phenylethynylcyclohexene-1 (II); this unsaturated hydrocarbon was oxidized with 75% acetyl hydroperoxide to form the oxide (III).

Treatment of the oxide with acetic acid gives the partial acetate, 1-phenylethynyl-2-acetoxy-1-cyclohexanol (IV), which, on saponification, with saturated aqueous sodium carbonate, forms the glycol, 1-phenylethynyl-cyclohexane-1,2-diol (V). The acetylenic glycol was also obtained by us by the action of water on the oxide.

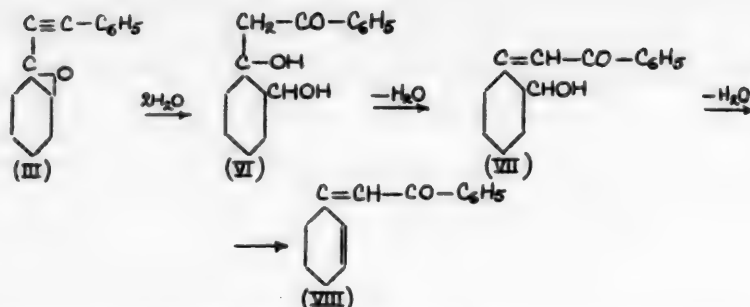


The acetylenic oxide was subjected to hydration by Kucherov's method. This reaction led to the unsaturated ketone, $\Delta^{2,3}$ -cyclohexylidene-acetophenone(VIII) which decolorizes bromine in chloroform, gives a positive reaction for carbonyl group with 2,4-dinitrophenylhydrazine, and does not manifest the presence of a hydroxyl group with methyl magnesium iodide.

The formation of the unsaturated ketone apparently proceeds in the following way: treatment of the oxide with mercuric sulfate solution results in addition of two molecules of water — one at the place of rupture of the oxide ring and the other at the acetylenic bond. At first a ketoglycol, 1,2-dihydroxycyclohexyl- ω -acetophenone (VI), is formed, and this then loses a molecule of water to give 2-hydroxycyclohexylidene-1-acetophenone (VII); the latter on dehydration changes into $\Delta^{2,3}$ -cyclohexylideneacetophenone (VIII). (See top of next page.)

We did not isolate the two intermediate products (VI and VII).

Simultaneous hydration and dehydration by the Kucherov reaction has also been observed by other authors.



Thus, Venus-Danilova and co-workers applied this method of hydration to 1-phenylethynyl-cyclopentan-1-ol [6] and 1-phenylethynyl-cyclohexan-1-ol [7] and obtained the unsaturated ketones cyclopentylidene-acetophenone and cyclohexylidene-acetophenone.

EXPERIMENTAL

Synthesis of 1-phenylethynyl-cyclohexan-1-ol. 102 g phenylacetylene (b.p. 140-142° at 731 mm) was condensed by Iotsich's method with 98 g cyclohexanone (b.p. 154-155° at 731 mm); a solid mass was obtained from which by two distillations (b.p. 124-125° at 0.5 mm) was isolated 146 g (73%) of a crystalline substance with m.p. 61-62°, in agreement with the data of Iotsich [8] who first synthesized this alcohol.

Dehydration of 1-phenylethynyl-cyclohexan-1-ol with potassium bisulfate. The reaction was effected by heating with fused KHSO_4 and simultaneous removal of the water formed in vacuum at 30° (40 mm). Dehydration of the alcohol was completed in 25 minutes. Yield of hydrocarbon, 1-phenylethynyl-cyclohexene-1, 90%.

B.p. 122-123° (0.5 mm), d_4^{20} 0.9929, n_D^{20} 1.6051. Pinkney [9] reports b.p. 117-118.5° (2 mm), d_4^{20} 0.9391, n_D^{20} 1.6033.

Oxidation of 1-phenylethynyl-cyclohexene-1 with acetyl hydroperoxide. To an ethereal solution of 51.6 g of the unsaturated hydrocarbon cooled to -7° was added, over a period of 2 hours, 75% acetyl hydroperoxide (diluted with ether) in the amount of 30 g, as calculated for one atom of oxygen per double bond.

The temperature of the reaction mass was kept at not higher than 0°. After addition of the whole of the acetyl hydroperoxide the reaction mixture was stood at room temperature. The course of the oxidation in the main and control experiments was checked by daily titration with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution. 1 ml of the main and of the control solution was diluted with water to 200 ml, and 25 ml of each was titrated.

From the data set forth we see that oxidation of 1-phenylethynyl-cyclohexene-1 by acetyl hydroperoxide took place over a period of 5 days.

Amount of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ (in ml) consumed in titration of unreacted acetyl hydroperoxide:

	1 day	2 days	3 days	4 days	5 days
Experiment	5.55	1.05	0.6	0.4	0.3
Control	5.55	5.35	5.0	4.8	4.7

In the course of this period the control showed a slight change of concentration of acetyl hydroperoxide. At the end of the period the reaction mixture was neutralized with 10% NaOH until its reaction was neutral. The ether layer was separated, dried for 24 hours with potassium carbonate and then filtered. The ether was driven off and the residue fractionated in vacuum. Two distillations gave 46 g (82%) substance with b.p. 144-145.5° (1 mm):

d_4^{20} 1.0581, n_D^{20} 1.5774, M_R 62.05; calculated 59.19.

0.1071 g substance: 0.3338 CO_2 ; 0.0722 g H_2O . 0.1276 g substance: 0.3979 g CO_2 ; 0.0830 g H_2O .

0.2790 g substance; 23.52 g benzene: Δt 0.315°. Found %: C 85.00, 85.03; H 7.54, 7.28; M 193.2.

$\text{C}_{14}\text{H}_{14}\text{O}$. Calculated %: C 84.85; H 7.13; M 198.

The prepared 1-phenylethynyl-cyclohexene-1 oxide dissolves readily in ethyl ether, ethyl alcohol and chloroform; it is insoluble in water.

Action of acetic acid on 1-phenylethynyl-cyclohexene-1 oxide. 5 g of the oxide was mixed with 11.5 g glacial acetic acid; the temperature rose to 35° during this operation. The mixture was refluxed on a water bath for 4 hours at 50-55° and then boiled for 2 hours. The unreacted acetic acid was distilled off and the residual mass was twice distilled to give a remarkably viscous, yellow liquid with b.p. 164-166° (5 mm) in amount of 3.1 g (48%).

b.p. 164-166° (0.5 mm); n_D^{20} 1.5538.

0.1045 g substance: 0.2854 g CO₂; 0.0675 g H₂O. 0.1013 g substance: 0.2776 g CO₂; 0.0673 g H₂O.

0.1178 g substance: 10.5 ml CH₄ (16°, 753 mm).

0.2564 g substance: 23.96 g benzene: Δt 0.218°. Found %: C 74.48, 74.73; H 7.22, 7.41; OH 6.38;

M 251.6. C₁₆H₁₈O₃. Calculated %: C 74.42; H 7.03; OH 6.59; M 258.

The data indicate that the substance is the partial acetate of a glycol, 1-phenylethynyl-2-acetyloxycyclohexanol-1. It is soluble in ethyl alcohol, ethyl ether, chloroform and benzene. It does not crystallize after standing for 45 days.

Hydrolysis of 1-phenylethynyl-cyclohexene-1 oxide. 6.7 g oxide was hydrolyzed with 40 ml water containing a trace of sulfuric acid with continuous shaking and heating on a water bath at 50° for 3 hours.

A viscous mass which adhered to the walls of the flask was formed. It was extracted with ether, washed with aqueous sodium carbonate solution and with water, and then dried for a day with sodium sulfate. The ether was driven off to leave a residue with a very high viscosity and a honey-like odor which did not distill in vacuum. The compound could not be crystallized from ethyl ether, ethyl alcohol, or benzene, nor did it crystallize after prolonged standing (40 days). Only after introduction of a crystal of the same substance, prepared by hydrolysis of the partial acetate of the glycol with saturated sodium carbonate solution, did it crystallize rapidly. The crystalline product was purified by dissolving it in ethanol and precipitating with water. After three repetitions of this operation, filamentous crystals were obtained with m.p. 82.5-83°, which did not give a depression in a mixed test with the crystals obtained by hydrolysis of the partial acetate.

0.1067 g substance: 0.3027 g CO₂; 0.0708 g H₂O. 0.1120 g substance: 0.3191 g CO₂; 0.0741 g H₂O.

0.0880 g substance: 17.5 ml CH₄ (16°, 751 mm). 0.1868 g substance: 15.78 g benzene: Δt 0.27°.

Found %: C 77.37, 77.70; H 7.42, 7.41; OH 14.18; M 224.4. C₁₄H₁₆O₂. Calculated %: C 77.78;

H 7.42; OH 15.74; M 216.

The substance analyzed is a glycol - 1 phenylethynyl-cyclohexane-1,2-diol - readily soluble in the above-mentioned solvents for the partial acetate of the glycol.

Hydration of 1-phenylethynyl-cyclohexene-1 oxide by Kucherov's method. To 10 g oxide was added, with good stirring and cooling to 0°, 30 ml of a solution of HgSO₄ (3.5 g HgSO₄, 25 ml conc. H₂SO₄, 75 ml water); heat was generated and the mixture acquired a yellow color and became viscous. After 20 minutes the cooling was stopped. The reaction proceeded violently and was accompanied by crackling and marked temperature rise. The mass acquired a brown-green color and became more mobile. It was extracted with ether, washed 3 times with water and dried for 24 hours with sodium sulfate. The ether was driven off and from the residue after two distillations was isolated 4.5 g (45%) mobile liquid:

B.p. 125-127° (0.5 mm), d_4^{20} 1.0890, n_D^{20} 1.6092, M_D 62.97; calculated 60.13.

0.0988 g substance: 0.3073 g CO₂; 0.0644 g H₂O. 0.1169 g substance: 0.3629 g CO₂; 0.0743 g H₂O.

0.2837 g substance: 23.70 g benzene: Δt 0.313. Found %: C 84.78, 84.67; H 7.29, 7.11; M 196.2.

C₁₄H₁₄O. Calculated %: C 84.85; H 7.13; M 198.

The prepared unsaturated ketone, $\Delta^{2,3}$ -cyclohexylidene-acetophenone, dissolves readily in ethyl ether and chloroform, less readily in ethyl alcohol, and is insoluble in water.

With 2,4-dinitrophenylhydrazine it forms a dark-red resinous precipitate which was recrystallized from boiling ethanol with addition of ethyl acetate. After cooling, a resinous precipitate again came down. It was treated with ethyl ether and a substance was thus obtained which melted in a sealed capillary at 119-121°.

0.1012 g substance: 12.4 ml N₂ (17.5°, 757.2 mm). 0.1320 g substance: 16.4 ml N₂ (17°, 761.5 mm).

Found %: N 14.25, 14.55. C₂₀H₁₈O₄N₄. Calculated %: N 14.81.

The analysis agrees with the formula for $\Delta^{2,3}$ -cyclohexylidene-acetophenone 2,4-dinitrophenylhydrazone.

SUMMARY

1. Oxidation of the unsaturated hydrocarbon 1-phenylethynyl-cyclohexene-1 with acetyl hydroperoxide gave its oxide in a yield of 82 %.

2. With acetic acid the oxide forms the partial acetate, 1-phenylethynyl-2-acetyloxy-cyclohexan-1-ol, which, on hydrolysis, gives the glycol, 1-phenylethynyl-cyclohexane-1,2-diol. This glycol is also obtained by the action of water on the oxide.

3. Hydration of the oxide by Kucherov's method gave the unsaturated ketone, $\Delta^{2,3}$ -cyclohexylidene-acetophenone.

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Received February 3, 1954

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* See Consultants Bureau English translation page 1193

** See Consultants Bureau English translation page 1561.

PREPARATION OF THE CYCLIC HYDRAZIDE OF MALEIC ACID AND OF SOME OF ITS DERIVATIVES

Yu. A. Baskakov and N. N. Melnikov

In recent years [1] the attention of investigators has been attracted by the singular physiological activity toward plants of the cyclic hydrazide of maleic acid, the systematic name of which is 1,2-dihydropyridazinedione-3,6. In low concentrations (0.01-0.025%) it retards the flowering of various plants or even entirely prevents it [2]; in higher concentrations (0.1-0.2%) maleic acid hydrazide causes temporary stoppage of the growth of plants [1] which property is exploited for delaying the germination of fruits and potatoes during storage over long periods [3-5]. It has been proposed to employ maleic acid hydrazide for treatment of lawns in place of mechanical cutting [6]. Depending upon the concentration of the preparation employed, the retardation of plant growth is effective over a longer or shorter period. Normally a consumption of 8-10 kg per hectare of maleic acid hydrazide can serve for combating certain weeds [7]. Great interest attaches to the application of maleic acid hydrazide for treatment of lemons with the aim of raising their frost resistance [8].

Notwithstanding the undoubted practical value of 1,2-dihydropyridazinedione-3,6 in agriculture, very little has been published about its preparation.

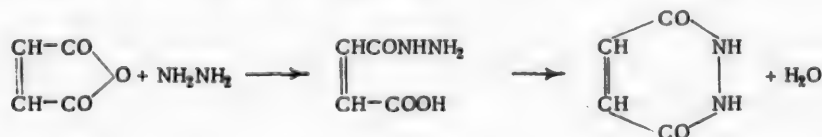
1,2-Dihydropyridazinedione-3,6 was first prepared in 1895 by Curtius [9] by reaction of hydrazine hydrate with maleic anhydride in ethanol. Under these conditions, however, the yield of 1,2-dihydropyridazinedione-3,6 did not exceed 50%. Curtius' method was later studied by Arndt, Loewe and Ergener [10] but they were unable to effect an appreciable improvement in the yield.

We commenced the study of maleic acid hydrazide as far back as 1950 in connection with its action on the physiological processes of plants. The publication in 1952 of an American patent [11] on the preparation of 1,2-dihydropyridazinedione-3,6 by reaction between hydrazine hydrochloride and maleic anhydride in aqueous solution prompted us to accelerate the publication of the present communication.

Our systematic study of the reaction of hydrazine hydrate and of hydrazine salts (of organic and inorganic acids) with maleic anhydride in aqueous solution showed that the yield of 1,2-dihydropyridazinedione-3,6 depends markedly on the final pH of the medium. The yield of 1,2-dihydropyridazinedione-3,6 rises in an acid medium and falls sharply if a strong acid is absent from the reaction medium. Good yields of 1,2-dihydropyridazinedione-3,6 (over 90%) can be obtained by starting both from salts by hydrazine with inorganic acids, and from hydrazine hydrate with addition to the reaction mixture of a small amount of a strong acid or of a salt of hydrazine with a strong acid. 1,2-Dihydropyridazinedione-3,6 can even be obtained in good yield by reaction with maleic anhydride of such poorly water-soluble salts as hydrazine sulfate.

With the objective of clarifying the mechanism of formation of 1,2-dihydropyridazinedione-3,6 and of verifying the general character of the dependence which we had discovered, we studied the reaction of hydrazine and of phenylhydrazine not only with maleic anhydride but also with the anhydrides of chloro-, dichloro-, bromo- and dibromomaleic acids, and with citraconic anhydride. In all these cases, the formation of cyclic hydrazides of the respective acids most easily proceeds in an acid medium, while the anhydrides of dihalomaleic acids only give cyclic hydrazides on heating with concentrated sulfuric acid.

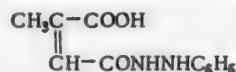
The data obtained indicate the possible mechanism of formation of 1,2-dihydropyridazinedione-3,6 and its derivatives. Formation of 1,2-dihydropyridazinedione-3,6 apparently proceeds in two stages: at first an acid hydrazide is formed which then cyclizes:



The first reaction proceeds in the cold with equimolecular amounts of reactants; the second proceeds with heating of the reaction mixture in presence of strong acids or of excess of maleic anhydride. Strong acids create

a high hydrogen ion concentration in the reaction mixture, this being necessary for suppression of the dissociation of the maleic acid and the intermediate acid hydrazide. The high hydrogen ion concentration also catalyzes the cyclization reaction with loss of a molecule of water. In the case of dihalomaleic anhydrides, as indicated above, cyclization only occurs on heating of the intermediate acid hydrazide with concentrated sulfuric acid, since dihalomaleic acids are considerably stronger than maleic acid and a non-aqueous medium is necessary for suppression of dissociation. Two isomeric forms of the phenylhydrazide of citraconic anhydride can exist: 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 and 1,2-dihydro-1-phenyl-4-methylpyridazinedione-3,6.

In our case it is most probable that 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 is formed since, according to Anschütz [12], the acid phenylhydrazide of citraconic acid has the structure:



The chloromaleic anhydride required for synthesis of the hydrazide was prepared by direct chlorination of maleic anhydride by a slight modification of the patented method [13]. The chloromaleic anhydride obtained by the latter method was found to be contaminated with a trace of maleic anhydride, from which the chloro compound is freed with difficulty by distillation.

Direct chlorination of chloromaleic anhydride also gave dichloromaleic anhydride in good yield, while bromination of maleic anhydride and bromomaleic anhydride led to satisfactory yields of bromo- and dibromomaleic anhydrides. These compounds are extremely difficult to prepare by the methods described in the literature.

All the substituted dihydropyridazinediones were tested for inhibition of growth of shoots of wheat, radish and hemp, and were found to be practically inactive in the concentration range of 0.01-0.5%.

EXPERIMENTAL

1. Preparation of chloromaleic anhydride. A stream of chlorine was passed through a mixture of 196 g maleic anhydride and 3 g iron powder at 105°. Chlorination went on for 10 hours, after which the temperature of the mixture was raised to 190° and heating was carried out at this temperature for 5-6 hours until hydrogen chloride ceased to come off. At the end of the reaction 220 g crude chloromaleic anhydride was distilled off from the reaction flask in the vacuum of a water jet pump. A second distillation in vacuum gave a fraction boiling at 106-110° (40 mm) containing an insignificant amount of the original maleic anhydride.

2. Preparation of dichloromaleic anhydride. Chlorination under the above-described conditions of 132 g chloromaleic anhydride in presence of 1.5 g iron powder gave 140 g (84%) dichloromaleic anhydride, m.p. 118° after recrystallization from ligroine.

3. Preparation of bromomaleic anhydride. 106 g bromine was gradually added at 80° to a mixture of 98 g maleic anhydride and 1 g iron powder which was irradiated with a 300-watt lamp. After all the bromine had been added, the mixture was heated at the same temperature and irradiated for another 8 hours, after which the temperature was raised to 120-130°. At this temperature the mixture was heated for 4 hours, and then the reaction product was distilled in the vacuum of a water jet pump. A fraction boiling at 150-152° (42 mm) was collected. Yield 120 g (68%).

4. Preparation of dibromomaleic anhydride. Under the above-described conditions 35.4 g bromomaleic anhydride, 0.5 g iron powder and 34 g bromine gave 35 g dibromomaleic anhydride (68.3%) with m.p. 114°.

5. Preparation of 1,2-dihydropyridazinedione-3,6. Starting compounds for the preparation were salts of hydrazine with hydrochloric, sulfuric and oxalic acids, hydrazine hydrate and maleic anhydride. In the latter case the catalysts used were small amounts of salts of sulfuric or oxalic acids or hydrazine hydrochloride.

In all cases the yield of 1,2-dihydropyridazinedione-3,6 was 85-95%.

The reaction was carried out under the following typical conditions: To a suspension of maleic anhydride in a small amount of water was added an aqueous solution of a hydrazine salt (excluding the poorly soluble hydrazine sulfate, which was added in the form of suspension), and after stirring for 30-40 minutes the reaction mixture was boiled for 1-3 hours. On cooling, the 1,2-dihydropyridazinedione-3,6 was filtered off and purified by recrystallization from water.

6. Preparation of 1,2-dihydro-4-chloropyridazinedione-3,6. The method described for maleic hydrazide was applied to a mixture of 26.5 g chloromaleic anhydride and 26 g hydrazine sulfate in 100 ml water.

There was obtained 26.5 g (90%) 1,2-dihydro-4-chloropyridazinedione-3,6. Traces of 1,2-dihydropyridazinedione-3,6 were removed by dissolving the crude reaction product in the calculated amount of dilute aqueous alkali and adding to the solution of the sodium salts a small amount of hydrochloric acid. The precipitated 1,2-dihydropyridazinedione-3,6 (with a trace of the main product) was filtered off; the 1,2-dihydro-4-chloropyridazinedione-3,6 was then brought down from the mother liquor by acidification with hydrochloric acid. The product was finally purified by recrystallization from water. M.p. 254° (with decomposition).

Found %: Cl 24.01, 23.68; M 147.6, 147.3. Calculated %: Cl 24.21; M 146.45.

7. Preparation of 1,2-dihydro-4-bromopyridazinedione-3,6. 31 g 1,2-dihydro-4-bromopyridazinedione-3,6 was obtained by the above method from 35.4 g bromomaleic anhydride and 26 g hydrazine sulfate in 150 ml water. M.p. 251° (with decomp.) after recrystallization from water.

Found %: Br 41.32, 41.24; M 192.15, 192.6. Calculated %: Br 41.84; M 190.9

8. Preparation of 1,2-dihydro-4,5-dichloropyridazinedione-3,6. 33.4 g dichloromaleic anhydride, 26 g hydrazine sulfate and 150 ml water were stirred in a three-necked flask at room temperature for an hour, and then with heating on a boiling bath for 2 hours. After cooling, the precipitate was filtered off, dried, and heated at 150° for an hour with ten times the weight (400 g) of 80% sulfuric acid. At the conclusion of the heating, the mixture was cooled and carefully run, with cooling, into twice the volume (800-1000 ml) of water. The precipitate was filtered and washed with a little cold water. Yield 25 g (68 %) 1,2-dihydro-4,5-dichloropyridazinedione-3,6. After recrystallization from water the substance had an m.p. of 296° (with decomp.).

Found %: Cl 38.46, 38.80; M 179.0, 179.3. Calculated %: Cl 39.20, M 180.9.

9. Preparation of 1,2-dihydro-4,5-dibromopyridazinedione-3,6. Using the method described for 1,2-dihydro-4,5-dichloropyridazinedione-3,6, 25.6 g dibromomaleic acid was reacted with 13 g hydrazine sulfate in 100 ml water to give 16 g (59.2%) 1,2-dihydro-4,5-dibromopyridazinedione-3,6. Two recrystallizations from a large volume of water gave the pure compound which darkens but does not melt at 330°.

Found %: Br 59.01, 58.81; M 271.2, 271.5. Calculated %: Br 59.23; M 269.8.

10. Preparation of 1,2-dihydro-4-methylpyridazinedione-3,6. From 22.4 g citraconic anhydride and 26 g hydrazine sulfate, using the method described for 1,2-dihydropyridazinedione-3,6, was obtained 24 g 1,2-dihydro-4-methylpyridazinedione-3,6 (95%). After recrystallization from water the compound melts at 278° (with decomp.).

Found M 125.7, 125.2. Calculated: M 126.1

11. Preparation of 1,2-dihydro-2-phenylpyridazinedione-3,6. 19.6 g maleic anhydride was mixed with 28.8 g phenylhydrazine hydrochloride in 300 ml water. To the mixture was added 30 ml conc. hydrochloric acid and it was then heated to the boil. At first a transparent solution was formed, but 5-10 minutes after the start of heating an abundant precipitate began to come down. Heating was continued for 2 hours, after which the mixture was cooled and filtered. The precipitate was washed on the filter with cold water and dried. Yield 30 g (80%). After recrystallization from water followed by treatment with activated carbon the pure substance was obtained with m.p. 261°.

Found M 190.4, 190.3. Calculated: M 188.18.

12. Preparation of 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6. From 16.8 g citraconic anhydride and 21.6 g phenylhydrazine hydrochloride in 250 ml water with addition of 20 ml hydrochloric acid was obtained 25 g (82.2%) substance. After recrystallization from water, 1,2-dihydro-2-phenyl-4-methylpyridazinedione-3,6 melts at 192°.

Found: M 202.0, 201.4. Calculated: M 202.2.

SUMMARY

1. A study was made of the reaction of maleic anhydride with hydrazine salts and hydrazine hydrate, using salts of hydrazine with strong acids. It was established that 1,2-dihydropyridazinedione-3,6 can be obtained in a yield of over 90% from maleic anhydride and hydrazine salts in an aqueous medium.

2. Starting from derivatives of maleic anhydride, a similar method was applied to the synthesis of a series of substituted cyclic hydrazides of maleic acid which had not previously been described in the literature.

3. A reaction mechanism is advanced for the formation of 1,2-dihydropyridazinedione-3,6 and its analogs from anhydrides and hydrazine salts.

4. All the synthesized substituted 1,2-dihydropyridazinedione-3,6 were found to be substantially inactive when tested on shoots of wheat, radish and hemp.

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Received February 4, 1954

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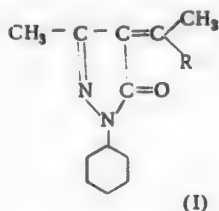
INVESTIGATIONS ON TAUTOMERIC COMPOUNDS

XVI. LABILITY OF THE HYDROGEN ATOMS IN THE PRODUCTS OF CONDENSATION OF PHENYLMETHYLPYRAZOLONE WITH KETONES

A.E. Porai-Koshits* and M.S. Dinaburg

The hydrogen atoms of the methylene group of phenylmethylpyrazolone are known to possess high lability. It appeared of interest to establish to what extent this lability is retained when the methyl group is separated from the heterocycle but is in the conjugated position to the latter.

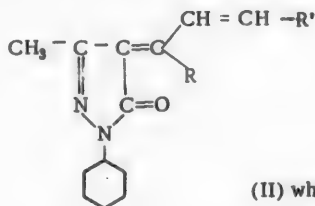
With this objective we made a study of the products of condensation of phenylmethylpyrazolone with ketones of the general formula (I) described in the previous communication [1]



One of us had previously shown [2] that as a criterion of the lability of the hydrogen atoms of methyl groups we may employ their ability to enter into reactions with aldehydes, nitroso compounds, and diazo compounds; it was established at the time that the reaction with aldehydes is the most general one, while compounds possessing extremely high activity of the hydrogen atoms react with diazo compounds; it was natural, therefore, that we should commence the investigation of compounds of type (I) by studying their reactions with aldehydes.

Experiments show that this reaction proceeds on heating the starting substances in alcoholic solution, and in many cases in the cold; deep ruby-red or violet-red crystalline products are obtained.

The properties of the prepared compounds, their color and their analytical data indicate that formula (II) should be assigned to them.



A comparison of the course of the reaction between aldehydes and various compounds of the type of (I) reveals that the facility with which the latter enter into reaction depends, under otherwise identical conditions, on the nature of the radical R entering the compound with the ketone residue. The most active is a derivative of m-nitroacetophenone (R = C₆H₄-m-NO₂); the least active is a derivative of acetone (R = CH₃). The latter is the compound with the least pronounced acidic properties, whereas in the acetophenone derivative the acidic properties are clearly manifested. Consequently we observe here a well-marked parallelism between the ability to condense with aldehydes and the acidity of the individual compounds.

On reacting 4-[α-m-nitrophenylethylidene]- and 4-[α-phenylethylidene]-phenylmethylpyrazolone with aldehydes, the yield of reaction products and the reaction velocity increase when traces of piperidine are present. Conversely, on condensation of aldehydes with isopropylidene-phenylmethylpyrazolone the presence of piperidine leads to complete breakdown of the methyl derivative, since the latter is distinguished by instability in presence of bases.

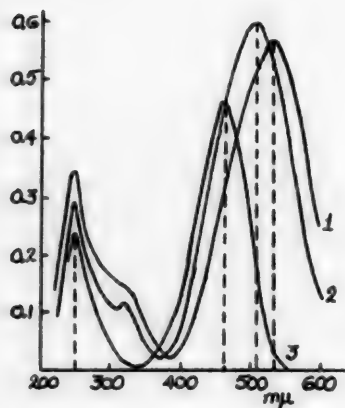
It might have been expected that 4-isopropylidene-phenylmethylpyrazolone would be capable of reacting with aldehydes through the hydrogens of both methyl groups. It was found, however, that only one of the methyl groups is capable of reacting with aldehydes. We may note that a similar phenomenon was observed in a study of

* Deceased.

the reaction of derivatives of isoxazolone [3] and dimethylfulvene with aldehydes [4]. It is evident that due to the distribution of the influence of the hetero atoms of the ring between two methyl groups, there is a considerable lowering of the activity of the hydrogen atoms in the methyl groups, and possibly even complete inactivation of one of them.

One of the authors in collaboration with Khromov [5] has shown, with reference to isoxazolone derivatives, that in a number of cases the action of aldehydes is accompanied by displacement of the ketone residue by the aldehyde with formation of the corresponding arylidene derivatives of isoxazolone. We did not observe the analogous reaction of displacement of ketones from the products of their condensation with phenylmethylpyrazolone even in the case of the least stable compound — isopropylidene-phenylmethylpyrazolone.

As already mentioned, the products of condensation of aldehydes with substances of the type of (I) which we obtained are deeply colored. We thought it would be interesting to compare the depth of their color with that of arylidene derivatives of phenylmethylpyrazolone not containing the dimethyl grouping. With this objective we determined their absorption spectra, which are shown in the diagram. The curves show that introduction of the dimethyl grouping into an arylidene derivative considerably shifts the absorption maximum in the direction of longer waves (compare Curves 1 and 3 in the figure).



1) 4-[α -(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone; 2) 4-[α -(p-dimethylaminostyryl)-ethylidene]-phenylmethylpyrazolone; 3) 4-dimethylaminobenzylidene-phenylmethylpyrazolone.

In addition to the absorption in the visible region of the spectrum, intense absorption is also observed in the ultraviolet with a maximum at $\lambda = 250 \text{ m}\mu$, which is characteristic both of phenylmethylpyrazolone itself and of many of its derivatives.

EXPERIMENTAL

4-[α -(o-Nitrostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared by 4-5 hours' boiling of 4.28 g isopropylidene-phenylmethylpyrazolone and 3.02 g o-nitrobenzaldehyde in 15 ml methanol. Yield 2.7 g (38.7%). Bright-red needles (from benzene).

0.1681 g substance: 0.4225 g CO_2 ; 0.0795 g H_2O ; 0.1507 g substance: 16.4 ml N_2 (18°, 762 mm). Found %: C 68.97, H 5.23; N 12.10. $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_3$. Calculated %: C 69.17; H 4.89; N 12.10.

4-[α -(p-Nitrostyryl)-ethylidene]-phenylmethylpyrazolone-5. Prepared in a similar way to the preceding compound by 5-hours' boiling. Yield 18.5%. Violet-brown needles from benzene, m.p. 171-172°.

0.1074 g substance: 11.25 ml N_2 (19°, 761 mm). Found %: N 12.25. $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_3$. Calculated %: N 12.10.

4-[α -(p-Dimethylaminostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared in the same way as before by 6-hours' boiling. Yield 26.9%, m.p. 178°. Violet-red needles (from a mixture of benzene and ligroine).

0.1431 g substance: 0.4019 g CO_2 ; 0.0879 g H_2O . 0.1714 g substance: 0.4797 g CO_2 ; 0.1034 g H_2O . 0.1259 g substance: 13.2 ml N_2 (19°, 761 mm). Found %: C 76.62, 76.30; H 6.71, 6.70; N 12.27. $\text{C}_{22}\text{H}_{23}\text{ON}_3$. Calculated %: C 76.52; H 6.66; N 12.17.

4-[α -(p-Chlorostyryl)-ethylidene]-phenylmethylpyrazolone. Prepared by boiling 2.14 g isopropylidene-phenylmethylpyrazolone, 1.4 g p-chlorobenzaldehyde and 10 ml methanol for 2½ hours. Yield 0.65 g (19.4%). Long brown-red needles from benzene, m.p. 154-155°.

0.1429 g substance: 10.35 ml N_2 (17°, 755 mm). Found %: N 8.51. $\text{C}_{20}\text{H}_{17}\text{ON}_2\text{Cl}$. Calculated %: N 8.34.

4-[α -(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. 5.52 g phenylethylidene-phenylmethylpyrazolone, 2.98 g p-dimethylaminobenzaldehyde, 10 ml methanol and 2 drops piperidine were boiled together. A precipitate appeared after 30 minutes. Yield 6.0 g (73.7%). Lustrous, nearly black needles (from alcohol). m.p. 210-211°.

In the absence of piperidine the yield after 1½ hours was 3.2 g (39.15%).

0.1600 g substance: 0.4688 g CO₂; 0.0903 g H₂O. 0.1565 g substance: 13.39 ml N₂ (19°, 761 mm). 0.1745 g substance: 15.50 ml N₂ (19°, 763 mm). Found %: C 79.89; H 6.26; N 10.26; 10.15. C₂₇H₂₅ON₃. Calculated %: C 79.00; H 6.14; N 10.30.

4-[α -(p-Dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. Preparation as for 4-[α -(p-dimethylaminostyryl)-benzylidene]-phenylmethylpyrazolone. Yield 63.0%. Green needles (from acetone), m.p. 167-168°.

0.1731 g substance: 0.5035 g CO₂; 0.1091 g H₂O. 0.1311 g substance: 0.3866 g CO₂; 0.0774 g H₂O. Found %: C 79.29, 80.46; H 6.79, 6.55. C₂₉H₂₉ON₃. Calculated %: C 80.00; H 6.68.

4-[α -(o-Nitrostyryl)-benzylidene]-phenylmethylpyrazolone. 1.38 g phenylethylidenephylmethylpyrazolone 0.76 g o-nitrobenzaldehyde, 5 ml methanol and 1 drop piperidine were boiled 30 minutes. Yield 1.14 g (55.8%). Blue-black leaflets from glacial acetic acid or acetone, m.p. 194-195°.

0.1551 g substance: 0.4188 g CO₂; 0.0697 g H₂O. 0.1618 g substance: 0.4344 g CO₂; 0.0754 g H₂O. 0.1567 g substance: 14.0 ml N₂ (18°, 762 mm). 0.1027 g substance: 9.4 ml N₂ (19°, 763 mm). Found %: C 73.64, 73.04; H 4.88, 5.16; N 10.44, 10.58. C₂₅H₁₉O₃N₃. Calculated %: C 73.25; H 4.64; N 10.27.

4-[α -(p-Chlorostyryl)-benzylidene]-phenylmethylpyrazolone. 2.76 g phenylethylidene-phenylmethylpyrazolone, 1.4 g p-chlorobenzaldehyde, 1 drop piperidine and 15 ml methanol were boiled 15 minutes. Yield 1.8 g (43%). Bright-red needles from acetone, m.p. 146-147°.

0.1001 g substance: 0.0372 g AgCl. 0.1197 g substance: 0.0411 g AgCl. 0.1288 g substance: 0.0480 g AgCl. Found %: Cl 8.43, 9.20, 8.54. C₂₅H₁₉OCl. Calculated %: Cl 8.90.

4-[α -(o,p-Dichlorostyryl)-benzylidene]-phenylmethylpyrazolone. Prepared like the preceding compound. Yield 67%, m.p. 155-156°. Ruby-red needles from acetone.

0.1653 g substance: 0.1161 g AgCl. 0.2046 g substance: 0.1333 g AgCl. Found %: Cl 16.27, 16.25. C₂₅H₁₈OCl₂. Calculated %: Cl 16.39.

4-[α -(m-Methoxy-p-hydroxystyryl)-benzylidene]-phenylmethylpyrazolone. 1.38 g 4-(α -phenylethylidene)-phenylmethylpyrazolone, 0.76 g 4-hydroxy-3-methoxybenzaldehyde, 8 ml methanol and 1 drop piperidine were boiled 12 minutes. Yield 1.4 g (68.4%). Violet-red leaflets from acetic acid, m.p. 220-221°.

0.1401 g substance: 8.5 ml N₂ (19°, 762 mm). Found %: 7.11. C₂₆H₂₂O₃N₂. Calculated %: N 6.83.

4-[α -(m-Hydroxystyryl)-benzylidene]-phenylmethylpyrazolone. Preparation as before. Yield 78.9%. Violet-red prisms from alcohol, m.p. 215°.

0.1831 g substance: 0.5269 g CO₂; 0.0934 g H₂O. 0.1366 g substance: 8.7 ml N₂ (17°, 748 mm). 0.1820 g substance: 11.5 ml N₂ (17°, 756 mm). Found %: C 78.90; H 5.57; N 7.59, 7.40. C₂₅H₂₀O₂N₂. Calculated %: C 78.90; H 5.26; N 7.40.

4-[α -Styrylbenzylidene]-phenylmethylpyrazolone. 3.12 g benzaldehyde, 5.52 g phenylethylidene-phenylmethylpyrazolone, 15 ml methanol and 1 drop piperidine were brought to the boil; the mass crystallized at once. Yield 3.7 g (50.8%). M.p. 173-174°. Prisms from glacial acetic acid.

0.1313 g substance: 0.3961 g CO₂; 0.0690 g H₂O. 0.1470 g substance: 10.3 ml N₂ (17°, 753 mm). Found %: C 82.20; H 5.83; N 7.82. C₂₅H₂₀ON₂. Calculated %: C 82.41; H 5.49; N 7.68.

4-[α -(p-Dimethylaminostyryl)-m-nitrobenzylidene]-phenylmethylpyrazolone. 12 g p-dimethylaminobenzaldehyde, 2.6 g 4-(α -m-nitrophenylethylidene)-phenylmethylpyrazolone, 20 ml ethyl alcohol and 1-2 drops piperidine were heated to the boil, when a dense crystalline precipitate immediately came down. This was filtered and the filtrate was further heated. A fresh crop of crystals appeared and was filtered off. Total yield 2.3 g (63%). Green, bronzing needles from aqueous acetone. M.p. 150-151°.

0.1097 g substance: 0.2878 g CO₂; 0.0566 g H₂O. 0.1297 g substance: 14.0 ml N₂ (20°, 760 mm). Found %: C 71.60; H 5.80; N 12.57. C₂₇H₂₄O₃N₃. Calculated %: C 71.68; H 5.51; N 12.38.

Condensation of 4-(α -phenylethylidene)-phenylmethylpyrazolone with aldehydes at the ordinary temperature

1) 2.76 g methyl derivative, 1.06 g benzaldehyde, and 2 drops piperidine were mixed with 5 ml methanol and left to stand at the ordinary temperature. The solid quickly dissolved and an hour later crystals came down from the dark-red solution. These were filtered after 16 hours, washed with methanol and dried. Yield 2.9 g (79.8%). M.p. 173-174°. Violet-red prisms from acetic acid, m.p. 174°.

2) Similar results were got when the above-described reaction was carried out in the absence of a solvent.

3) 1.38 g 4-(α -phenylethylidene)-phenylmethylpyrazolone, 0.75 g p-dimethylaminobenzaldehyde, 2 drops piperidine and 10 ml methanol were stood for 3 days. The precipitated blue-black crystals were filtered off, washed with cold methanol and dried. Yield 1.89 g (93%). M.p. 209-211°.

4) In a similar manner the reactions with all the above-mentioned aldehydes can be realized.

Attempt to condense 4-isopropylidene-phenylmethylpyrazolone with 2 moles p-dimethylaminobenzaldehyde.
2.14 g (0.01 mole) 4-isopropylidene-phenylmethylpyrazolone, 2.98 g (0.02 mole) p-dimethylaminobenzaldehyde and 10 ml methanol were refluxed 6 hours. On cooling, a crystalline precipitate came down; it was filtered and washed with cold alcohol. One crystallization from 75% ethyl alcohol gave colorless leaflets, m.p. 70-72°, identified as p-dimethylaminobenzaldehyde. The dark-colored mother liquor did not crystallize after separation of the aldehyde. It was diluted with water; the oil which separated was decanted and twice extracted with boiling water. From the aqueous layer was obtained a further 0.37 g p-dimethylaminobenzaldehyde. The oil did not crystallize in the course of a long period, and only after complete drying-out of the water present did it form crystals. They were pressed to remove oil, and formed small violet needles, m.p. 174-176° (after two crystallizations from a mixture of benzene and ligroine).

SUMMARY

1. The products of condensation of phenylmethylpyrazolone with methylketones possess an extremely high lability of the hydrogen atoms in the methyl groups.

Due to the lability of the hydrogen atoms of the methyl groups, they are capable of reacting with aldehydes, forming deeply colored dimethyl derivatives.

2. Unlike the majority of compounds containing mobile hydrogen atoms, the products of condensation of phenylmethylpyrazolone with ketones can react with aldehydes even in the cold.

3. The reaction with aldehydes is catalyzed by piperidine in those cases when the original methyl derivative is stable to the action of bases.

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Received December 18, 1953

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* T.p. = C.B. Translation pagination.

SCISSION OF CARBON-CARBON BONDS UNDER THE INFLUENCE OF DIAZO COMPOUNDS*

I. REACTION OF SOME TERTIARY AMINES OF THE TRIPHENYLMETHANE SERIES WITH DIAZO COMPOUNDS

V. V. Perekalin and L. P. Popova

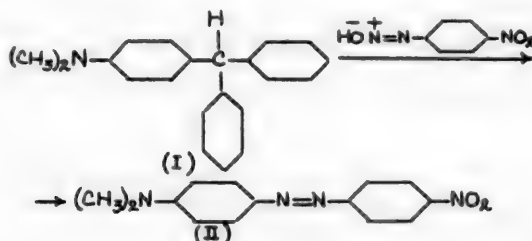
In the literature are described numerous cases of rupture of the bonds between carbon atoms, as well as between atoms of carbon and sulfur, halogens and nitrogen, occurring under the influence of diazo compounds in aromatic and more rarely in aliphatic-aromatic compounds.

In this reaction the molecule reacting with the diazo compound is cleaved, and the diazo compound residue takes the place of the part of the molecule which it displaces (for example sulfo groups [1-5], the bromine atom [6], the azo group [7], the carboxyl group [8-12], the propenyl residue [13] and the methylol group [14]). This displacement occurs when the substituent in the molecule is in the position at which the diazo group would have entered if the substituent in question had been absent, i.e. during the normal course of the azo-coupling reaction; usually this is the ortho- or para-position of the aromatic nucleus in relation to the groups promoting the reaction of azo-coupling (for example ortho or para to the dimethylamino group or the hydroxyl group).

We have investigated the character of the reaction with diazo compounds (p-nitrodiazobenzene and diazobenzene) of some tertiary amines of the triphenylmethane and diphenylmethane series.

As a rule, when carrying out these reactions aqueous solutions of the diazo compounds are added to aqueous solutions of salts of the amines (addition is made more rarely to their alcoholic solutions or aqueous suspensions); the precipitated azo dye (when the cleavage reaction takes place) was separated from the solution which was either subjected to the action of fresh portions of diazo compound or else the original amines and the products of their cleavage were isolated from it.

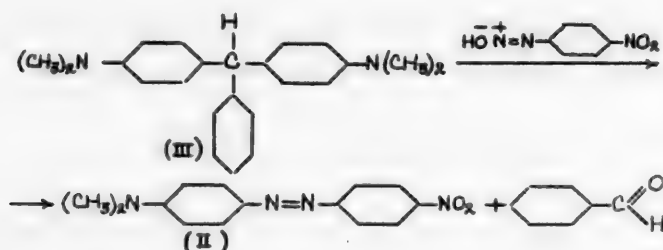
The simplest tertiary amine of the triphenylmethane series, 4-dimethylaminotriphenylmethane (I), was cleaved with difficulty when coupled in an aqueous alcoholic medium with p-nitrodiazobenzene and formed the azo dye 4-dimethylamino-4'-nitroazobenzene (II) from the residues of dimethylaniline and p-nitrodiazobenzene. At the same time the starting amine not entering into the reaction separated out. The second product of cleavage - diphenylcarbinol - was not isolated.



4,4'-Tetramethyldiaminotriphenylmethane (leuco base of malachite green) (III) was subjected to treatment with 1 and 2 moles of p-nitrodiazobenzene and also to stepwise reaction with the latter: after coupling with one mole of diazo compound and removal of the resultant azo dye, the solution was treated with a second mole of p-nitrodiazobenzene. In each case scission of the leuco base took place without difficulty; the products of scission were formed in high yield and the azo dye (II) was isolated in high yield.

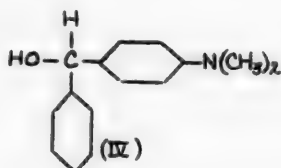
* Submitted at the sitting of the Leningrad Division of the Mendeleev All-Union Chemical Society on April 9, 1953; at the same time a communication on very similar investigation was published by E. Ziegler and G. Snatzke [15].

Treatment of base (III) with 1 mole p-nitrodiazobenzene caused partial scission with formation of 1 mole of azo dye (II) and benzaldehyde (isolated as the dimedon derivative), and there remained the non-reacted base which was oxidized to malachite green.



Reaction of (III) with 2 moles diazo compound led to its complete scission; 2 moles of the azo dye (II) and benzaldehyde were isolated.

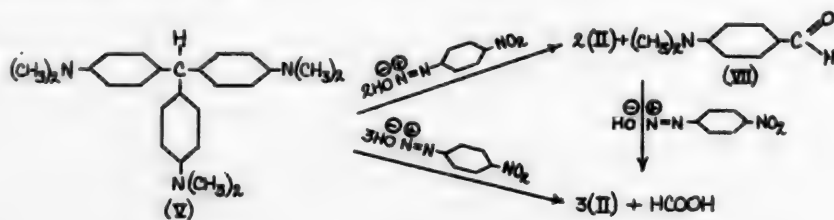
An intermediate product of the scission of (III) was possibly 4-dimethylaminodiphenylcarbinol (IV) which reacts further with the diazo compound with formation of azo dye (II) and benzaldehyde. The absence of (IV) from the products of scission of (III) may be explained in two ways: 1) carbinol (IV) in an acidic medium is converted into the original leuco base and benzaldehyde*; the rate of interaction of p-nitrodiazobenzene with carbinol (IV) is higher than the velocity of the reaction of p-nitrodiazobenzene with the leuco base (III). However, special experiments on the action on (IV) of hydrochloric acid under conditions resembling those during azo-coupling (in the cold), and also on heating, did not confirm the first hypothesis: the original carbinol was isolated quantitatively; hence the second hypothesis is apparently valid.



4,4',4''-Hexamethyltriaminotriphenylmethane (leuco base of crystal violet) (V) was treated with 1, 2 and 3 moles of p-nitrodiazobenzene, and was also subjected to stepwise treatment in succession with 3 moles of the diazo compound.

Reaction of base (V) with 1 mole diazo compound causes partial scission, the products being azo dye (II) and formic acid, while part of the base remains unchanged and is recovered after oxidation to crystal violet.

Action of 2 moles diazo compound on (V) led to synthesis of 2 moles of azo dye (II) and to formation of 4-dimethylaminobenzaldehyde (VII).



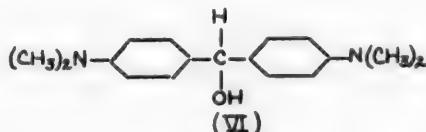
* A similar conversion, although under more drastic conditions, was observed by A.E. Porai-Koshits for carbinols of the antipyrine series [16].

Reaction with 3 moles p-nitrodiazobenzene resulted in complete scission with formation of 3 moles azo dye (II) and formic acid.

TABLE 1
Yield of Azo Dye Formed on Scission of Amines of the Triphenylmethane Series with p-Nitrodiazobenzene

Amine	No. of moles of p-nitrodiazobenzene	Yield of azo dye (II) in % of theoretical
4-Dimethylaminotriphenylmethane (I)	1	30
4,4'-Tetramethyldiaminotriphenylmethane (III)	1	99.6
	2	92.8
4,4',4''-Hexamethyltri-aminotriphenylmethane (V)	1	85.8
	2	87.0
	3	86.4

In the reaction of (V) with 1 mole diazo compound the intermediate product was 4,4'-tetramethyldiamino-diphenylcarbinol (VI); its absence from the reaction products may be explained by the higher velocity of its scission in comparison with that of the original leuco base. The hypothesis of disproportionation of carbinol (VI) to base (V) and aldehyde (VII) was not confirmed experimentally. Formation of (VII) during reaction of (V) with 2 moles diazo compound is clear evidence of the lower velocity of its scission in comparison with that of (VI).



The dyes malachite green and crystal violet, obtained by oxidation of leuco bases (III) and (IV), did not undergo modifications under the influence of different amounts of p-nitrodiazobenzene; the positions of the long-wave maxima on the absorption curves before and after treatment with the diazo compounds were identical. The p-nitrodiazobenzene not entering into reaction was bound by 2-naphthol (Table 2). Hydrolysis of aqueous solutions of the dyes, which could have led to formation of carbinol bases, was inhibited by addition of weak hydrochloric acid solutions of the diazo compounds.

EXPERIMENTAL

1. Reaction of 4-dimethylaminotriphenylmethane (I) [17] with p-nitrodiazobenzene

a) Scission did not occur in aqueous hydrochloric acid solution, the original amine being quantitatively recovered; the diazo compound was converted into an azo dye by coupling with 2-naphthol [18].

b) In an alcoholic medium. To a solution of 0.29 g (I) in 30 ml ethyl alcohol was added 10 ml 0.1 N solution of p-nitrodiazobenzene in the course of an hour at 10-12°. After 10 hours the precipitate was filtered; it consisted of 4-dimethylamino-4'-nitroazobenzene (azo dye II). M.p. 229°; a mixed test with an authentic specimen of azo dye (II) (m.p. 230° [19]) gave m.p. 229°. Yield 0.8 g (30%). From the filtrate, after dilution with twice the amount of water and rendering alkaline with 25% ammonia solution, was isolated 0.13 g (45%) of the original amine. M.p. 130°.

2. Reaction of 4,4'-tetramethyldiazminotriphenylmethane (III) with 1 mole of p-nitrodiazobenzene.

a) Azo coupling and isolation of the azo dye. To a solution of 3.3 g leuco base in 200 ml water containing a very slight excess of hydrochloric acid (an excessive amount of hydrochloric acid slows down the reaction) was added 100 ml 0.1 N solution of p-nitrodiazobenzene in the course of an hour with stirring at 5-10°. The first few drops of diazo solution imparted a red color to the solution, and a dark-red, finely granular precipitate gradually began to come down; after 10 hours the azo dye was filtered off. M.p. 228-229°; a mixed test with a specimen of authentic azo dye (II) did not give a depression. Yield 2.69 g (99.6%).

b) Isolation of non-reacted leuco base by oxidation to malachite green. To the filtrate, acidified with 1.6 ml 37% hydrochloric acid solution and 0.8 ml 60% acetic acid, was added in small portions at 0° with stirring 1 g lead dioxide mixed with 10 ml water; the mixture was stirred 5 hours and then filtered. To the filtrate was added 0.82 zinc chloride, dissolved in a little water, and a saturated sodium chloride solution. After 24 hours the malachite green in the form of a double salt was filtered off. Yield 1.3 g (51.7%) dye. The positions of the long-wave maxima of the absorption curves of the dye obtained by oxidation of the leuco base and of malachite green were identical (λ 618 m μ).

c) Isolation of benzaldehyde. The benzaldehyde was distilled off with steam from the filtrate (after removal of the azo dye) and extracted from the distillate with ether. After removal of the ether it was dissolved in 10 ml alcohol and stirred with a solution of 1.4 g dimedon in 50 ml 50% aqueous ethyl alcohol. The solution was heated on a boiling water bath for 30 minutes and cooled. The dimedon derivative of benzaldehyde came down; m.p. 193°. A mixed test with the authentic dimedon derivative (m.p. 194° [20]) had m.p. 193°; yield 0.7 g (40% calculated on the assumption that 0.5 mole leuco base had undergone scission).

3. Reaction of (III) with 2 moles p-nitrodiazobenzene

a) Azo coupling and separation of the dye. Azo coupling was carried out as described in 2a.

To a solution of leuco base was added 200 ml 0.1 N p-nitrodiazobenzene solution; azo dye (II) came down. M.p. 229°; yield 5 g (92.8%).

b) Separation of benzaldehyde. The procedure was the same as in 2c. The dimedon derivative had m.p. 193°; yield 2.65 g (75%).

4. Reaction of 4,4',4''-hexamethyltriaminotriphenylmethane (V) with 1 mole of p-nitrodiazobenzene

a) Azo coupling and isolation of the azo dye. To a solution of 3.73 g leuco base in 10 ml 10% hydrochloric solution, diluted to 200 ml with water, was added 100 ml 0.1 N p-nitrodiazobenzene solution at 5-10° with stirring in the course of an hour. After 10 hours the azo dye (II) was filtered off. M.p. 229° Yield 2.32 g (85.8%).

b) Isolation of unreacted leuco base and qualitative determination of formic acid. The original leuco base came down when the filtrate was made alkaline with 25% ammonia solution. M.p. 162.5°; a mixed sample with the authentic leuco base (m.p. 170°) melted at 165°. Yield 2.28 g (89.3%) of base (calculated on the assumption that 0.35 mole original substance had reacted). The ammoniacal solution was acidified with 10% sulfuric acid solution and distilled. Addition to the distillate of an ammoniacal solution of silver oxide and heating on a water bath caused separation of a black precipitate of metallic silver.

c) Isolation of unreacted leuco base by oxidation to crystal violet. Addition was made to the filtrate, freed from azo dye, of 5 ml 37% hydrochloric acid; after boiling 15-20 minutes, cooling and filtering, the crystal violet was salted out with sodium chloride. After 10 hours 1.66 g dye was filtered off (61% calculated on the assumption that 0.35 mole original leuco base had entered into reaction). The positions of the long-wave maxima of the absorption curves of the dye obtained by oxidation of the leuco base and of crystal violet were identical (λ 690 m μ).

5. Reaction of (V) with 2 moles p-nitrodiazobenzene

a) Azo coupling and isolation of the dye. Azo coupling was carried out as described in 2a; to a solution of leuco base was added 200 ml 1 N p-nitrodiazobenzene solution in the course of 3 hours; yield of diazo dye (II) 4.7 g (87%).

b) Isolation of 4-dimethylaminobenzaldehyde (VII). 1) In the free state. Compound (VII) was isolated from the filtrate by treatment with a few milliliters of 25% ammonia solution. M.p. 72°; a mixed test with an authentic specimen of the aldehyde did not give a depression. Yield 6.9 g (61.5% on the assumption that 0.66 mole leuco base entered into reaction). 2) In the form of the dimedon derivative. The dimedon derivative of 4-dimethylaminobenzaldehyde was isolated from the filtrate (freed from azo dye). M.p. 192°; a mixed test with an authentic specimen of the dimedon derivative [20] did not give a depression. Yield 2.56 g (62% calculated for reaction of 0.66 mole leuco base).

6. Reaction of (V) with 3 moles p-nitrodiazobenzene

Azo coupling was effected as described in 4a; to a solution of the leuco base was added 300 ml 0.1 N p-nitrodiazobenzene solution in the course of 3 hours; 7.0 g (86.4%) azo dye (II) was isolated. Formic acid was detected in the filtrate by the method described in 4b.

7. Reaction of malachite green (oxalic acid salt) with 1 mole p-nitrodiazobenzene

4.05 g dye was dissolved at 60-70° in 300 ml water, and the solution was coded and filtered. To the dye solution was added 100 ml acidified p-nitrodiazobenzene solution in the course of an hour with stirring at 5-10°. After 10 hours the mixture was filtered to give 3.5 g (86.5%) of starting dye. The filtrate, containing unreacted p-nitrodiazobenzene, was added to a solution of 1.44 g 2-naphthol in 100 ml 1% NaOH solution; 4-nitro-1-benzeneazo-2-naphthol came down with m.p. 250° (from benzene); a mixed melting point test with the authentic azo dye did not give a depression.

Experiments in the reaction of malachite green and crystal violet with, respectively, 2 and 1, and 2 and 3 moles p-nitrodiazobenzene proceeded under analogous conditions and their results are set forth in Table 2.

TABLE 2

Reaction of malachite green and crystal violet with p-nitrodiazobenzene

Dye	Taken for reaction		Isolated			
	Dye (g)	p-Nitro-diazobenzene (moles)	original dye		4'-nitro-1-benzeneazo-2-naphthol	
			g	% of starting dye	g	% of theoretical
Malachite green	4.05	1	3.5	86.5	2.65	90.4
	4.05	2	3.0	74.1	5.5	93.8
Crystal violet	4.08	1	3.8	93.1	2.7	93.0
	4.08	2	3.2	78.4	5.2	88.7
	4.08	3	3.2	78.4	7.5	85.7

The positions of the long wave maxima of the absorption curves of malachite green and crystal violet were unchanged before and after treatment with p-nitrodiazobenzene and were respectively 618 and 500 m μ .

SUMMARY

1. It was shown that tertiary amines of the triphenylmethane series containing the dimethylamino group in the para-position to the methane bond undergo scission under the influence of active diazo compounds so that the carbon-carbon bond between the methane carbon atom and the carbon atoms of the benzene ring is broken.
2. It was established that one of the products of scission (the dimethylaniline residue) is bound by the diazo compound with formation of an azo dye, while the other separates in the free state (benzaldehyde, 4-methylaminobenzaldehyde, formic acid).
3. The ease of scission of the triphenylmethane nucleus increases with increasing number of dimethylamino groups (from one to two and three).
4. The hypothesis is advanced that certain products of scission (4-dimethylamino-diphenylcarbinol and 4,4'-tetramethyldiamino-diphenylcarbinol) were not isolated because the speed of their scission was higher than that of the original amines (leuco bases of malachite green and crystal violet).
5. It is shown that malachite green and crystal violet differ from their leuco bases in remaining unchanged under the action of diazo compounds.
6. The susceptibility to scission depends both on the structure of the amine and on the activity of the diazo compound; only active diazo compounds (p-nitrodiazobenzene) bring about cleavage.

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Received September 29, 1953

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SCISSION OF CARBON-CARBON BONDS UNDER THE INFLUENCE OF DIAZO COMPOUNDS

II. REACTION OF SOME TERTIARY AMINES OF THE DIPHENYLETHANE SERIES AND OF DIMETHYLANILINE DERIVATIVES WITH DIAZO COMPOUNDS

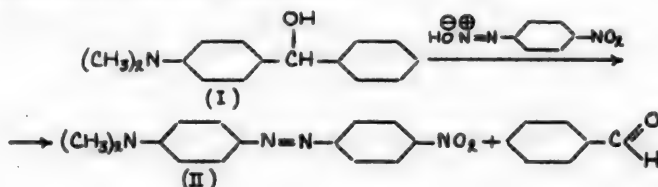
V. V. Perekalin, L. P. Popova and T. I. Abramovich

In the preceding communication [1] it was shown that reaction of leuco bases of malachite green and crystal violet with p-nitrodiazobenzene leads to derivatives of dimethylaniline, and that the intermediate products may be 4,4'-dimethylamino-diphenylmethane and 4,4'-tetramethyldiamino-triphenylmethane.

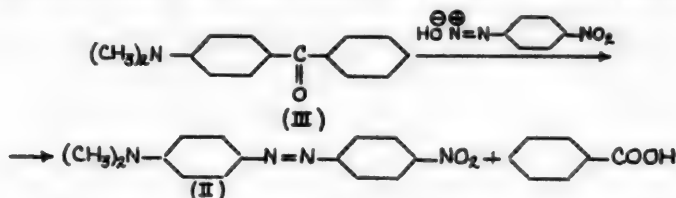
In order to obtain a more fundamental insight into the mechanism of the reaction under investigation, a systematic study has been undertaken of the reaction of some tertiary amines of the diphenylmethane series and of dimethylaniline derivatives with p-nitrodiazobenzene and, in some cases, with diazobenzene.

The experimental procedure was described in the previous communication [1].

4-Dimethylamino-diphenylcarbinol (I) (suggested intermediate product of scission of the leuco base of malachite green) on coupling with 1 mole of p-nitrodiazobenzene readily undergoes scission with formation of the azo dye 4-dimethylamino-4'-nitroazobenzene (II) and benzaldehyde.



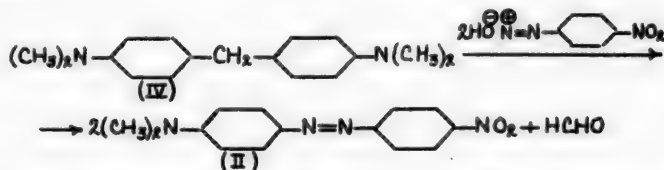
Scission of 4-dimethylamino-diphenylketone (III) proceeds with greater difficulty than that of carbinol (I). Low yields of the azo dye (II) and benzoic acid were obtained, and a small amount of the unreacted ketone was recovered.



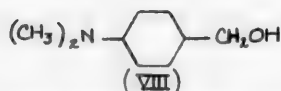
4,4'-Tetramethyldiaminodiphenylmethane (IV), as shown by Sharvin and Kalyanov [2], is cleaved by two moles of p-sulfodiazobenzene with formation of the azodye 4-dimethylamino-(4'-sulfo)-diazobenzene and formaldehyde.

A more detailed investigation of the scission of amine (IV) showed that scission is incomplete when using 1 mole of diazo compound (p-nitrodiazobenzene): the products are 1 mole azo dye and formaldehyde (collected in the form of the dimedon derivative), and part of the original amine remains unchanged.

Under the influence of two moles of diazo compound, amine (IV) undergoes complete scission and forms 2 moles azo dye and formaldehyde.

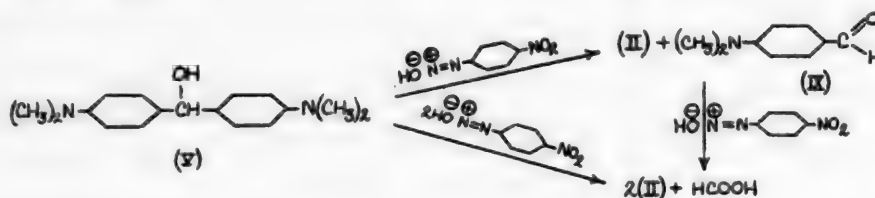


The intermediate product of the scission of (IV) is 4-dimethylaminobenzyl alcohol (VIII), which is not detected among the reaction products,

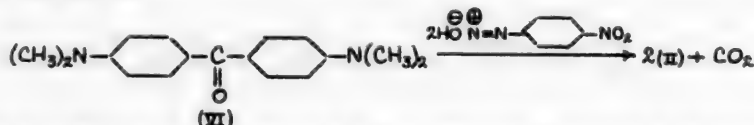


apparently due to the velocity of its scission being greater than that of the original amine (IV).

4,4'-Tetramethyldiamino-diphenylcarbinol (V) (hypothetical intermediate product of the scission of the leuco base of crystal violet), as reported in the literature [3], reacts with diazo compounds. With 1 mole p-nitrodiazobenzene it forms 1 mole azo dye (II) and 4-dimethylaminobenzaldehyde (IX); with 2 moles diazo compound 2 moles of azo dye (II) and formic acid are formed.



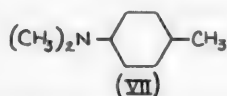
4,4'-Tetramethyldiaminodiphenyl ketone (VI) reacts with great difficulty with 2 moles of p-nitrodiazobenzene to give a low yield of azo dye (II).



Attention should be directed to the similarity in the character of the reaction of the leuco bases of malachite green and crystal violet (see [1]) and of 4,4'-tetramethyldiaminodiphenylmethane (IV) with diazo compounds:

- 1) 1 mole diazo compound cleaves only a part (0.5 mole) of the original amount of amine and forms 1 mole of azo dye.
- 2) The carbinol compounds (I), (V) and (VIII) are intermediate products of the scission of these amines.
- 3) 2 moles diazo compound bring about complete scission of the original amine so that 2 moles of azo dye and the corresponding aldehydes are formed.

It is a striking fact that 4-dimethyltoluidine (VII) is not cleaved by diazo compounds,



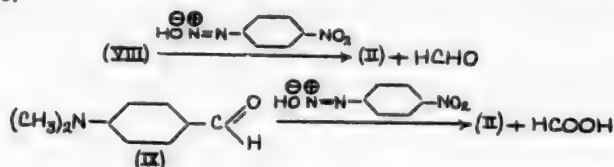
and can not undergo with them the azo-coupling reaction in the ortho-position to the dimethylamino group. *

Yield of Azo Dye Formed by Scission of Amines of the Diphenylmethane Series and of Some Derivatives of Dime; thylaniline by p-Nitrodiazobenzene.

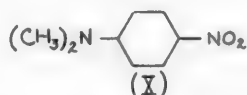
Amine	number of moles of p-nitrodiazobenzene	Yield of 4-dimethylamino-4'-nitroazobenzene (II) (in % of the theoretical)
4-Dimethylaminodiphenyl carbinol (I)	1	92.6
4-Dimethylaminodiphenyl ketone (III)	1	95.0
4,4'-Tetramethyldiaminodiphenylmethane (IV)	1	92.0
	2	75.6
4,4'-Tetramethyldiaminodiphenyl carbinol (V)	1	95.7
	2	89.3
4,4'-Tetramethyldiaminodiphenyl ketone (VI)	2	35.0
4-Dimethylaminobenzyl alcohol (VIII)	1	74.0
4-Dimethylaminobenzaldehyde (IX)	1	55.0

* This anomalous behavior of amine (VII) is apparently associated with the property of dimethylaniline and of some of its derivatives of coupling only in the para-position to the dimethylamino group, and requires special evaluation.

4-Dimethylaminobenzyl alcohol (VIII) behaves altogether differently in the azo-coupling reaction. Unlike amine (VII), it is easily cleaved by p-nitrodiazobenzene with formation of the azo dye and formaldehyde. Scission of 4-dimethylaminobenzaldehyde (IX) by the diazo compound proceeds with somewhat greater difficulty, but there is no doubt at all that scission takes place.



On the other hand, 4-dimethylamino-4'-nitrobenzene (X) does not react with p-nitrodiazobenzene in spite of variations in the reaction conditions, although easy scission of 4-dimethylaminobenzoic acid has been reported in the literature [2].



All the compounds that we investigated were subject to the action of p-nitrodiazobenzene. A less active diazo compound - diazobenzene - did not cause scission of these compounds.

The reaction medium plays an important part; excess of mineral acid leads to formation of amine salts which inhibit and sometimes stop the scission reaction.

EXPERIMENTAL

1. Reaction of 4-dimethylaminodiphenyl carbinol (I) [4] with p-nitrodiazobenzene

a) In aqueous hydrochloric acid solution. To a solution of 0.227 g carbinol in 1 ml 10% hydrochloric acid and 10 ml water, neutralized with 10% sodium acetate solution in such a manner that the reaction was weakly acidic and the whole of the carbinol remained in solution, was added 10 ml 0.1 N p-nitrodiazobenzene solution at 5-10° with stirring in the course of an hour. On adding the diazo compound the solution turned red and azo dye (II) gradually came down; this was filtered after 10 hours. M.p. 228-229°; a mixed melting point test with an authentic specimen of dye (II) (m.p. 229°) gave m.p. 229°. Yield 0.26 g (92.6%). The filtrate was distilled with steam and the distillate treated with ether; the benzaldehyde remaining after removal of the ether was dissolved in 2 ml alcohol and mixed with a solution of 0.28 g dimedon in 10 ml 50% aqueous ethyl alcohol. The dimedon derivative of benzaldehyde with m.p. 193.5° separated after heating the mixture for 30 minutes on a water bath; a mixture with the authentic derivative (m.p. 194.5°) had m.p. 194.0°. Yield 0.17 g (46.3%).

b) In an alcoholic medium. To a solution of 0.227 g carbinol (I) in 25 ml ethyl alcohol was added 100 ml 1 N p-nitrodiazobenzene solution in the course of 2 hours; after 2 hours azo dye (II) was filtered off; yield 0.26 g (99.6%). From the filtrate was isolated the dimedon derivative of benzaldehyde; yield 0.16 g (44%).

2. Reaction of 4-dimethylaminodiphenyl ketone (III) [5] with p-nitrodiazobenzene

Coupling of 1.13 g ketone (III), dissolved in 80 ml ethyl alcohol, with 25 ml of 0.2 N solution of p-nitrodiazobenzene gave the azo dye (II) which was filtered off after 10 hours. M.p. 229°; yield 0.35 g (25%). 0.8 g (62%) of the original ketone was isolated from the filtrate after dilution with three times its amount of water and making alkaline with 25% ammonia solution; m.p. 89-90°; no depression in mixed melting test. The filtrate, freed from ketone, was acidified with 10% hydrochloric acid solution and treated with ether. Benzoic acid was separated from the ethereal extract. M.p. 116-117°; a mixture with authentic benzoic acid (m.p. 121°) had m.p. 118-119.

3. Reaction of 4,4'-tetramethyldiaminodiphenylmethane (IV) [6] with 1 mole of p-nitrodiazobenzene

After coupling 2.54 g amine (IV), dissolved in 7.5 ml 10% hydrochloric acid and diluted with water to a volume of 100 ml, with 100 ml 0.1 N p-nitrodiazobenzene solution, azo dye (II) was isolated (after 10 hours). M.p. 228°; yield 2.48 g (92%). The filtrate was made alkaline with 25% ammonia solution to bring down the original amine with m.p. 87° in amount of 1 g (78% on the assumption that 0.5 mole had entered into reaction). The filtrate after removal of the amine was distilled with steam. Formaldehyde was isolated from the distillate in the form of the dimedon derivative with m.p. 188°; a mixture with the authentic dimedon derivative (m.p. 189°) had m.p. 188°.

4. Reaction of amine (IV) with 2 moles p-nitrodiazobenzene

Coupling was carried out as described in section 3 above. To a solution of the amine was added 200 ml 0.1 N solution of p-nitrodiazobenzene. Azo dye (II) came down. M.p. 229°; yield 4.05 g (75%). The filtrate was steam-distilled and from the distillate was isolated the dimedon derivative of formaldehyde. M.p. 189°; yield 0.5 g (17%).

5. Reaction of 4,4'-tetramethyldiaminodiphenylcarbinol (V) [7] with 1 mole p-nitrodiazobenzene

To a solution of 2.7 g carbinol (V) in 0.75 ml 10% hydrochloric acid, diluted with water to 100 ml, was added 100 ml 0.1 N p-nitrodiazobenzene solution; after 10 hours azo dye (II) was filtered off. M.p. 228°; yield 2.59 g (95.7%). Neutralization of the filtrate with ammonia solution brought down 4-dimethylaminobenzaldehyde with m.p. 72.5°; no depression in admixture with the authentic aldehyde. Yield 0.3 g (42%).

6. Reaction of carbinol (V) with 2 moles of p-nitrodiazobenzene

Azo dye (II) was isolated by the procedure describe in Part 5. M.p. 229°; yield 4.8 g (89.3%). The filtrate was neutralized with 10% NaOH solution, acidified with 10% sulfuric acid and distilled. Formic acid was detected in the distillate by the ammoniacal silver oxide test.

7. Reaction of 4,4'-tetramethyldiaminodiphenyl ketone (VI) with 1 mole of p-nitrodiazobenzene

Azo dye (II) separated after coupling 2.68 g ketone (VI), dissolved in 300 ml ethyl alcohol, with 50 ml 0.2 N p-nitrodiazobenzene solution. M.p. 228-229° (after many recrystallizations from benzene); yield 1.62 g (30%). From the filtrate, diluted with 300 ml water and made alkaline with 25% ammonia solution, was isolated 1.2 g ketone (VI) (45% of the original amount). M.p. 171°; no depression in mixed melting test.

8. Reaction of ketone (VI) with 2 moles of p-nitrodiazobenzene

Azo dye (II) was isolated with m.p. 228-229° (yield 1.62 g; 30%) and the original ketone with m.p. 171° (1.7 g; 60% of the original amount).

9. Reaction of 4-dimethylaminobenzyl alcohol (VIII) [8] with p-nitrodiazobenzene

1.51 g alcohol (VIII) was dissolved in 5 ml 10% hydrochloric acid solution and the volume made up to 50 ml with water; addition was made of 5 ml 0.2 N p-nitrodiazobenzene solution; after 10 hours azo dye (II) was filtered off. M.p. 228°; yield 2 g (74%). From the filtrate was isolated, by the method of Part 3, the dimedon derivative of formaldehyde with m.p. 185-186°; a mixture with the authentic dimedon derivative (m.p. 188) had m.p. 187°.

10. Reaction of 4-dimethylaminobenzaldehyde (IX) with p-nitrodiazobenzene

To 1.49 g aldehyde (IX) in 3.6 ml 10% hydrochloric acid solution and 100 ml water was added 100 ml 0.1 N p-nitrodiazobenzene solution with stirring at 10-12° over a period of 2 hours; after 10 hours azo dye (II) was filtered off. M.p. 227°; yield 1.92 g (70.6%). Formic acid was detected in the filtrate by the method described in Part 6.

SUMMARY

1. It is shown that certain tertiary amines of the diphenylmethane series and some derivatives of dimethylaniline containing the dimethylamino group in the para-position to the methane bond undergo scission under the influence of active diazo compounds (p-nitrodiazobenzene); in this reaction the carbon-carbon bonds between the methane carbon atoms and the carbon atoms of the benzene rings are ruptured.

2. It was established that one of the products of scission (the dimethylaniline residue) is bound by the diazo compound with formation of an azo dye, while the other product separates in the free state (benzaldehyde, benzoic acid, formaldehyde, p-dimethylaminobenzaldehyde, formic acid).

3. The presence of only one dimethylamino group in diphenylmethane does not suffice for scission; introduction of a second dimethylamino group into the other benzene ring markedly increases the susceptibility to scission.

4. Replacement of a hydrogen atom by a hydroxyl group in the methane residue does not hinder the scission reaction; conversion of the carbinol residue into carbonyl hinders this reaction.

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Received September 29, 1953

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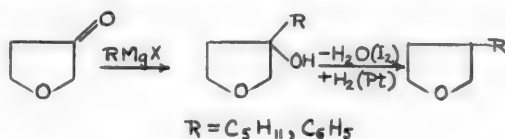
β-TETRAHYDROFURANONE AND THE SYNTHESIS OF β-ALKYL AND β-ARYLTETRAHYDROFURANS

Yu. K. Yuryev, E. M. Lukina and I. K. Korobitsyna

Up to recent times the preparation of β-alkyl- or β-aryltetrahydrofurans has been a difficult problem because the starting substances are difficultly accessible in each of the two known general methods of synthesis of these compounds. One of these methods – dehydration of the corresponding 1,4-diols – was used by Harries [1] for preparation of β-methyltetrahydrofuran and by Longinov [2] for preparation of β-propyl- and β-isohexyltetrahydrofuran. The second method – reaction of β-bromotetrahydrofuran with alkylolithiums – has been studied by one of us [3] and has been applied to the preparation of β-ethyl-, β-propyl- and β-butyltetrahydrofurans (it was impossible to obtain β-methyltetrahydrofuran by this method).

In 1952 one of us in collaboration with Korobitsyna and Savina [4] oxidized β-hydroxytetrahydrofuran with sodium bichromate and sulfuric acid in ethereal solution and obtained the corresponding ketone β-tetrahydrofuranone, which could serve as starting substance for the organomagnesium synthesis of β-alkyl- and β-aryltetrahydrofurans. In this connection we have improved the method for its preparation. A higher yield of β-tetrahydrofuranone was obtained by oxidizing β-hydroxytetrahydrofuran with sodium bichromate and sulfuric acid in aqueous solution at 0°, and it was also shown that it enters normally into reaction with organomagnesium compounds to give the corresponding tertiary alcohols.

By reacting β-tetrahydrofuranone with n-amyl magnesium chloride and with phenyl magnesium bromide, we obtained good yields of β-hydroxy-β-n-amyltetrahydrofuran and of β-hydroxy-β-phenyltetrahydrofuran respectively.



Consequently the reaction which we have described between β-tetrahydrofuranone and organomagnesium compounds is a convenient general method of synthesis of β-alkyl- and β-aryltetrahydrofurans.

EXPERIMENTAL

1. β-Tetrahydrofuranone. 88 g (1 mole) β-hydroxytetrahydrofuran (b.p. 81-82° at 13 mm, n_D^{20} 1.4530, d_4^{20} 1.1036) [5] and 50 ml water were placed in a three-necked flask fitted with mechanical stirrer, dropping funnel and reflux condenser. Addition was made, with cooling with ice water and stirring, of a solution (cooled to 0°) of 100 g (0.34 mole) sodium bichromate in 250 ml water and 75 ml concentrated sulfuric acid at a rate of 2 ml per minute. After addition of the whole of the chromic mixture, cooling was stopped and stirring was continued at room temperature. Heat was liberated by the reaction mass. The mixture was stirred for another 2 hours (following fall of the temperature to room temperature), left overnight, and then extracted many times with ether. The ethereal extracts were dried with potassium carbonate.

Removal of the ether followed by three fractional distillations of the residue gave 24.2 g β-tetrahydrofuranone:

B.p. 139-140° (760 mm); n_D^{20} 1.4384; d_4^{20} 1.1124; MR_D 20.21. $C_4H_6O_2$. Calculated MR_D 20.12.

Semicarbazone (from alcohol): m.p. of semicarbazone 164.5-165.5°.

Literature data: b.p. 139.4-139.8° (760 mm); n_D^{20} 1.4384; d_4^{20} 1.1124; m.p. of semicarbazone 164-165°.

21.0 g unchanged β-hydroxytetrahydrofuran was also isolated. Consequently the yield of β-tetrahydrofuranone was 28% of the theoretical calculated on the substance introduced into the reaction, and 37% calculated on the amount of reacted β-hydroxytetrahydrofuran.

No success attended attempts to prepare β-tetrahydrofuranone by catalytic dehydrogenation of β-hydroxytetrahydrofuran in presence of copper or by oxidation with atmospheric oxygen in presence of copper oxide.

2. β -Hydroxy- β -n-amyltetrahydrofuran. To an ethereal solution of n-amyl magnesium chloride, prepared from 4.9 g (0.2 mole) magnesium in 100 ml ether and 21.3 g n-amyl chloride, was added (with cooling to -10 to -12° and energetic stirring) a solution of 17.2 g (0.2 mole) β -tetrahydrofuranone in 20 ml ether.

After removal of the freezing mixture, the reaction mass was stirred for 2 1/2 hours at room temperature, heated 15 minutes on a water bath, left overnight, and decomposed with ice and ammonium chloride. After separation of the ethereal solution, the aqueous solution was repeatedly extracted with ether. The combined ethereal extracts were washed with water and dried with potassium carbonate.

The ether was driven off and the residue distilled twice to give 14.5 g (46%) β -hydroxy- β -n-amyltetrahydrofuran. The latter is a colorless liquid, with odor of mushrooms, highly soluble in ether and alcohol.

B.p. $112-112.5^\circ$ (3 mm) n_D^{20} 1.4557; d_4^{20} 0.9609; MR_D 44.74. $C_9H_{18}O_2$. Calculated MR_D 44.73.

Found%: C 68.64, 68.47; H 11.50, 11.55. $C_9H_{18}O$. Calculated %: C 68.31; H 11.47.

The number of hydroxyl groups was determined by the method of Terentyev and Kupletskaya [6].

Found%: OH 10.86, 10.86. $C_9H_{17}O(OH)$. Calculated %: OH 10.76.

β -Hydroxy- β -n-amyltetrahydrofuran has not been described in the literature.

3. β -n-Amyldihydrofuran. 14 g β -hydroxy- β -n-amyltetrahydrofuran was boiled 1.5 hours with 0.02 g iodine, and the solution was then slowly distilled from a flask with a small column.

After removal of the water, the distillate was dried with anhydrous sodium sulfate and fractionated in vacuum to give 7 g β -n-amylidihydrofuran:

B.p. $62.5-65.5^\circ$ (10 mm) n_D^{20} 1.4530; d_4^{20} 0.8844; MR_D 42.56. $C_9H_{16}O$. Calculated MR_D 42.74.

The product of dehydration decolorized bromine water and potassium permanganate solution.

4. β -n-Amyltetrahydrofuran. 8.5 g β -n-amylidihydrofuran was dissolved in 10 ml anhydrous ethyl alcohol and hydrogenated in presence of platinum oxide [7] in the cold with shaking. 1345 ml hydrogen (NTP) was absorbed (calculated 1518 ml).

The admixed unsaturated compound was removed by treating the product of hydrogenation with a solution of bromine in chloroform under cooling until a permanent yellow color had developed. It was then left overnight.

After driving off the chloroform, the residue was fractionated in vacuum (over sodium) to give 4.2 g (49%) β -n-amyltetrahydrofuran with the following constants:

B. p. $69-70^\circ$ (12 mm) n_D^{20} 1.4378; d_4^{20} 0.8602; MR_D 43.31. $C_9H_{18}O$. Calculated MR_D 43.20.

Found %: C 75.67, 75.60; H 12.55, 12.52. $C_9H_{18}O$. Calculated %: C 75.92; H 12.74.

β -n-Amyltetrahydrofuran is not described in the literature.

5. β -Hydroxy- β -phenyltetrahydrofuran. To phenyl magnesium bromide, prepared from 39.2 g (0.25 mole) bromobenzene in 120 ml ether, was added (with cooling to -10 to -12° and with stirring) an ethereal solution of 21.5 g (0.25 mole) β -tetrahydrofuranone. The reaction mass was stirred for 3.5 hours at room temperature and then left overnight. The reaction product was isolated in the manner described above.

23.5 g (57%) β -hydroxy- β -phenyltetrahydrofuran was isolated. It is a colorless, slightly mobile liquid, soluble in ether and alcohol.

B.p. $124-124.5^\circ$ (3 mm); n_D^{20} 1.5548; d_4^{20} 1.1567; MR_D 45.54. $C_{10}H_{12}O_2$. Calculated MR_D 45.74.

Found %: C 72.92, 72.93; H 7.47, 7.46. $C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.30.

β -Hydroxy- β -phenyltetrahydrofuran has not been described in the literature.

6. β -Phenyldihydrofuran. 18 g β -hydroxy- β -phenyltetrahydrofuran was dehydrated by boiling with iodine followed by distillation, when the main bulk came over at $240-242^\circ$ (758 mm). Vacuum distillation gave 13.2 g (81%) β -phenyldihydrofuran with b.p. $98.5-102^\circ$ (5 mm) and m.p. $39.5-40^\circ$; honey-like odor.

7. β -Phenyltetrahydrofuran. 10 g β -phenyldihydrofuran in 20 ml anhydrous alcohol was hydrogenated in presence of platinum oxide in the cold with shaking. 1410 ml (NTP) hydrogen was taken up (calculated 1540 ml).

Two fractional distillations over sodium gave 7 g (70%) β -phenyltetrahydrofuran with the following constants:

B.p. 81.5-82.5° (4 mm); n_D^{20} 1.5442; d_4^{20} 1.0448; MR_D 44.78. $C_{10}H_{12}O$. Calculated MR_D 44.22.

Found %: C 81.27, 81.19; H 8.15, 8.32. $C_{10}H_{12}O$. Calculated %: C 81.08; H 8.11.

β -Phenyltetrahydrofuran is a colorless, oily liquid, soluble in alcohol, ether and acetone; it has not been reported in the literature.

SUMMARY

The preparation of β -n-amyltetrahydrofuran and of β -phenyltetrahydrofuran (neither of which are described in the literature) showed that the reaction between β -tetrahydrofuranone and organomagnesium compounds is a convenient general method of synthesis of β -alkyl- and β -aryltetrahydrofurans.

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Received January 28, 1954

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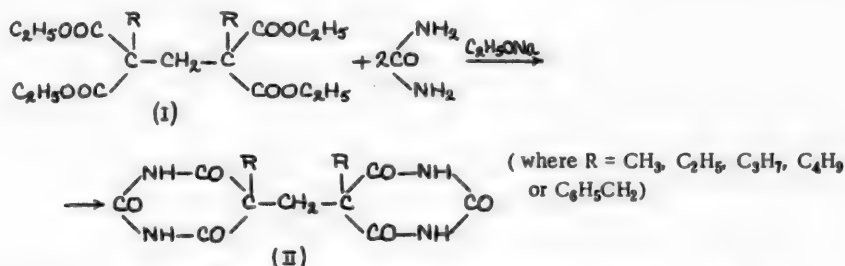
BARBITURIC ACIDS

I. SYNTHESIS OF METHYLENE-BIS-5-ALKYLBARBITURIC ACIDS

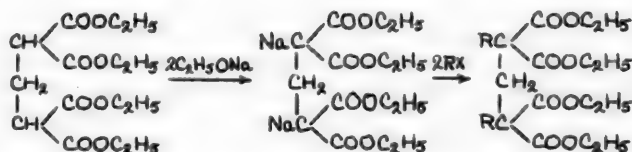
R. Ya. Levina and N. N. Godovikov

Methylene-bis-barbituric acid and its homologs had not been described in the literature until recently; it was only in 1949 that Gisling and Schwarzenbach [1] prepared methylene-bis-barbituric acid by reduction of methyl-bis-barbituric acid as well as by the usual method – the action of urea on methylene-bis-malonic ester in presence of sodium ethoxide.

In the present research, a series of previously undescribed methylene-bis-5-alkyl-barbituric acids (II) was synthesized by the action of urea on methylene-bis-alkylmalonic esters (I).

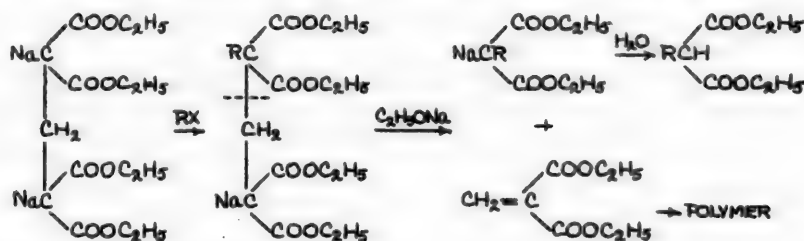


The starting methylene-bis-alkylmalonic esters were prepared by reaction of primary halides with methylene-bis-sodium malonic esters:



The yield of dialkyl esters was 20-40% of the theoretical. Secondary products of the reaction, isolated in all cases, were the corresponding monoalkylmalonic esters (in yields of 11 to 40% of the theoretical calculated on the methylene-bis-malonic ester) and the crystalline polymer of methylenemalonic ester, first described by N. D. Zelinsky [2].

Formation of these substances may be the result of scission of the intermediately formed sodium derivative of the monoalkylated methylene-bis-malonic ester under the action of sodium ethoxide, with formation of sodium alkylmalonic ester and methylenemalonic ester which is later transformed into the crystalline polymer *:



* A paper by Welch [3] draws attention to the possibility of such a scission. The author considered that on distillation in presence of caustic alkali, methylene-bis-malonic ester itself is cleaved with formation of malonic ester and methylenemalonic ester.

It should be noted that when using secondary bromides (iso-C₃H₇Br) or primary bromides with a branched structure (iso-C₄H₉Br; iso-C₅H₁₁Br) the reaction proceeded only according to the second scheme and the main reaction products were monoalkylmalonic esters (yields up to 53% of the theoretical); dialkylated methylene-bis-malonic esters were not formed.

Alkylation of methylene-bis-malonic ester has been described by Dressel [4] but without information about the yields of the alkylation products and their constants; his paper makes no mention of the formation of secondary products of reaction—monoalkylmalonic esters and the polymer of methylenemalonic ester.

EXPERIMENTAL

Methylene-bis-malonic ester was prepared in a yield of 60-70% of the theoretical by reaction of malonic ester with paraform in presence of 10% alcoholic KOH solution [3].

B.p. 174-175° (5 mm); n_D^{20} 1.4425; d_4^{20} 1.119 MR_D 78.57. Calculated MR_D 78.08.

Literature data [5]: b.p. 192° (12 mm); d_4^{20} 1.116.

Methylene-bis-malonic ester was characterized as the crystalline mercury derivative.

Mercuration of methylene-bis-malonic ester (0.01 mole) with mercuric acetate (0.02 mole) was effected by the method described for mercuration of ethyl malonate [6]. The resultant viscous oil was separated from the aqueous layer and dissolved in dilute alcohol. After addition of an aqueous solution of KCl, a white precipitate of the dichloro-mercuri-derivative came down. After recrystallization from a mixture of alcohol and acetone the methylene-bis-chloromercurimalonic ester (not described in the literature) melted at 165-167° with decomposition.

8.450 mg sub.: 6.760 mg CO₂; 2.150 mg H₂O; 6.950 mg sub.: 5.520 mg CO₂; 1.740 mg H₂O. Found %: C 21.83, 21.68; H, 2.84, 2.80. C₁₅H₂₂O₈Hg₂Cl₂. Calculated %: C 21.43; H 2.76.

Alkylation of methylene-bis-malonic ester

To sodium ethoxide (4.6 g Na in 150 ml anhydrous ethyl alcohol) was added methylene-bis-malonic ester (34 g, 0.1 mole) in small portions, followed dropwise (with stirring and heating on a water bath) by 0.3 mole alkyl halide (RX = CH₃I, C₂H₅Br, C₃H₇Br, C₄H₉Br, C₆H₅CH₂Cl). As soon as the reaction commenced, which was visible from the formation of a white precipitate of sodium halide, heating was stopped and only resumed after the whole of the alkyl halide had been added. The reaction mass was further heated for several hours until the alkaline reaction (to litmus) had almost completely disappeared. The alcohol was then distilled off and water was added to the residue; the oily layer was separated; the aqueous layer was extracted 3 times with ether, and the ether extracts added to the oil layer. The whole of the ethereal solution was washed with water and dried with calcium chloride; after driving off the ether the residual oil was distilled in vacuum.

Below are set forth the results obtained in each alkylation experiment.

1. Methylene-bis-methylmalonic ester. Three main fractions were obtained from the product of reaction between methylene-bis-sodium malonic ester and methyl bromide after fractional distillation in vacuum:

The 1st fraction (2.0 g, b.p. 78-79° at 10 mm; n_D^{20} 1.4132), judging by its constants was a secondary product of the reaction—monomethylmalonic ester (yield 11.5% of the theoretical calculated on the methylene-bis-malonic ester).

Literature data [7]: b. p. 201.2-201.4°; $n_D^{18.7}$ 1.4137.

From the 2nd fraction (14.0 g, b.p. 170-175° at 10 mm), after standing for a week and addition of a few drops of ether, was isolated 1.0 g (5%) polymer* of methylenemalonic ester with m.p. 156° (literature data [8]: m.p. 154-156°). The oil remaining after removal of the ether was unreacted methylene-bis-malonic ester (b.p. 174-175° at 5 mm; n_D^{20} 1.4430).

The third fraction was methylene-bis-methylmalonic ester, 11.1 g (30.8%).

B. p. 190-191° (10 mm); n_D^{20} 1.4470.

Literature data [4]: b.p. 191-192° (12 mm).

Since the close-boiling original methylene-bis-malonic ester might have been present as impurity in the prepared methylene-bis-methylmalonic ester, we purified the latter by the mercuration reaction.

* Methylmalonic ester readily polymerizes to a crystalline substance with m.p. 156°, to which is attributed the structure of a polymer containing 10-11 structural units [9].

To the methylene-bis-methylmalonic ester (fraction boiling at 190-191° at 10 mm) was added a solution of mercuric acetate in distilled water. The mixture was boiled 6 hours, and after cooling aqueous KCl solution was run in; a small amount of white precipitate came down (methylene-bis-chloromercurimalonic ester). The purified methylene-bis-methylmalonic ester was extracted with ether, the ether was driven off, and the dried residue was vacuum-distilled: b.p. 198-200° (17 mm), n_D^{20} 1.4460.

2. Methylene-bis-ethylmalonic ester. Two main fractions were got by vacuum distillation after reaction between methylene-bis-sodium malonic ester and ethyl bromide:

1st fraction [5.3 g (30.5%); b.p. 74-75° at 3 mm; n_D^{20} 1.4152], judging by its constants, was monoethylmalonic ester (literature data [10]; b.p. 77° at 5 mm), which was identified by transformation into ethylmalonic acid *

From the 2nd fraction (19 g; b.p. 164-175° at 3 mm) was isolated 8 g (22%) crystalline methylene-bis-ethylmalonic ester with m.p. 62-63° after recrystallization from dilute alcohol (literature data [4]; m.p. 61°).

To the non-crystallizing oil was added a few drops of ether; by this method it was possible to separate 1.2 g (7%) of the polymer of methylenemalonic ester with m.p. 154-156°, sparingly soluble in ether. The residue after removal of the ether was distilled in vacuum at 173-175° (5 mm) had n_D^{20} 1.4420, i.e. it was the original methylene-bis-malonic ester.

3. Methylene-bis-propylmalonic ester. Three fractions were collected, after two fractionations, from the product of reaction of methylene-bis-malonic ester with propyl bromide:

The 1st fraction [6.8 g (32.3%); b.p. 114-116° at 3 mm and n_D^{20} 1.4198] was propylmalonic ester. Literature data [12]; b.p. 222-227° (750 mm). Its hydrolysis gave a 70% yield of propylmalonic acid with m.p. 96° (from benzene). Literature data [13]; m.p. 96°.

Addition of ether to the 2nd fraction brought down 2.5 g polymer of methylene malonic ester with m.p. 154-155°. The residue after separation of the polymer was the original methylene-bis-malonic ester.

The 3rd fraction (17.0 g; b.p. 206-208° at 11 mm) crystallized completely; after recrystallization from aqueous alcohol, methylene-bis-propylmalonic ester was obtained with m.p. 41-42°. Yield 40% of the theoretical. Literature data [4]; m.p. 41-42°.

In this experiment, therefore, in contrast to the result of the experiment with ethyl bromide, it was possible to isolate the product of alkylation of the original methylene-bis-malonic ester by fractional distillation.

4. Methylene-bis-butylmalonic ester. Fractional distillation of the product of reaction between methylene-bis-malonic ester and butyl bromide gave 3 fractions:

The first fraction was monobutylmalonic ester, 6.6 g (30.0%):

B. p. 124-128° (18 mm); n_D^{20} 1.4229. Literature data [14]; b.p. 122° (12 mm); n_D^{20} 1.4222.

Addition of ether to the second fraction (6.2 g; b.p. 140-178° at 5 mm) brought down 2.7 g (15.0%) polymer of methylmalonic ester with m.p. 155-156°. The oil remaining after removal of the ether was the original methylene-bis-malonic ester (b.p. 174-175° at 5 mm; n_D^{20} 1.4420).

Redistillation of the third fraction (20.5 g; b.p. 185-205° at 5 mm) gave 14.0 g (37.4%) methylene-bis-butylmalonic ester in the form of a viscous oil with b.p. 198-199° at 5 mm; n_D^{20} 1.4522 (not described in the literature).

8.650 mg sub.: 19.672 mg CO₂; 6.932 mg H₂O. 4.540 mg sub.: 10.380 mg CO₂; 3.682 mg H₂O. Found %: C 62.00, 62.31; H 8.96, 9.16. C₂₃H₄₀O₈. Calculated %: C 62.13; H 9.06.

5. Methylene-bis-benzylmalonic ester. Two fractionations in vacuum of the product of reaction between methylene-bis-malonic ester and benzyl chloride gave 4 fractions.

The first fraction (7.8 g) was unreacted benzyl chloride:

B. p. 54-55° (4 mm); n_D^{20} 1.5408.

From the 2nd fraction (7.8 g; b.p. 145-180° at 4 mm) was isolated 3.5 g (20%) polymer of methylenemalonic ester with m.p. 155-156°; the residue was unchanged methylene-bis-malonic ester with b.p. 172-175° (5 mm); n_D^{19} 1.4430.

* Hydrolysis of ethylmalonic ester was effected by heating for 3 hours with alcoholic KOH (0.4 g, 10 ml alcohol). The alcohol was driven off and the residue dissolved in water; after 3 extractions, the aqueous layer was acidified with hydrochloric acid; the ethylmalonic acid formed was extracted with ether and the ether was evaporated; the residual oil crystallized after standing for 3 days. Yield 0.5 g (70%). After recrystallization from benzene the acid melted at 110-111°. Literature data [11]; m.p. 110-111°.

The third fraction (15 g; b.p. 210-240° at 4 mm) apparently contained, judging by the boiling point, dibenzylmalonic ester. Literature data [16]: b.p. 234° (23 mm).

Cooling of the 4th fraction (12.0 g; b.p. 240-250° at 4 mm) with solid carbon dioxide yielded 8.5 g (17%) crystals of methylene-bis-benzylmalonic ester with m.p. 44° after recrystallization from aqueous alcohol.

Methylene-bis-benzylmalonic ester had not previously been obtained in a crystalline form (literature data [4]: b.p. 200-250° in vacuum).

5.300 mg sub.: 13.175 mg CO₂; 3.410 mg H₂O. 5.965 mg sub.: 14.815 mg CO₂; 3.750 mg H₂O. Found %: C 67.83, 67.77 H 7.20, 7.03. C₂₃H₃₆O₈. Calculated %: C 67.95; H 7.02

6. Alkylation of methylene-bis-sodium malonic ester with secondary halides and with primary halides of branched structure (isopropyl, isobutyl and isoamyl bromide, also cyclohexyl chloride) did not lead to formation of normal products of reaction — methylene-bis-alkylmalonic esters. In all cases the main reaction was cleavage of the original methylene-bis-malonic ester: products isolated were the corresponding monoalkylmalonic esters, the crystalline polymer of methylenemalonic ester, and unreacted methylene-bis-malonic ester. The constants and yields of the monoalkylmalonic esters and the data in the literature are set forth in Table 1.

TABLE 1

Constants of monoalkylmalonic esters RCH(COOC₂H₅)₂

R	Boiling point	n _D ²⁰	Yield (in % of theoretical)	Literature data	
				Boiling point	n _D ²⁰
C ₃ H ₇ -iso	86-88° (5 mm)	1.4190	64.0	211-215° [15]	1.4180 [15]
C ₄ H ₉ -iso	101-103 (7 mm)	1.4282	64.7	118-120 (14 mm) [16]	—
C ₅ H ₁₁ -iso	133-135 (14 mm)	1.4243	58.3	160-165 (44 mm) [15]	1.4254 [15]
C ₆ H ₁₁	134-136 (4 mm)	1.4340	18.1	163-165 (20 mm) [17]	—

Methylene-bis-5-alkylbarbituric acids

To sodium ethoxide (1.4 g sodium in 30 ml anhydrous alcohol) was added 2.4 g (0.04 mole) urea followed by 0.01 mole methylene-bis-alkylmalonic ester. The reaction mixture was heated on an oil bath at 120° for 18 hours, after which the alcohol was distilled off and the residue dissolved in water. The aqueous solution was extracted 3 times with ether and then acidified with concentrated hydrochloric acid until it had an acidic reaction. The precipitate which came down on cooling with ice and salt was filtered off and recrystallized from aqueous alcohol. All the prepared barbituric acids are poorly soluble in water and in organic solvents.

When preparing methylene-bis-5-alkylbarbituric acids containing butyl and benzyl radicals there was isolated an oil as well as the crystalline barbituric acids. This oil has not yet been investigated more closely.

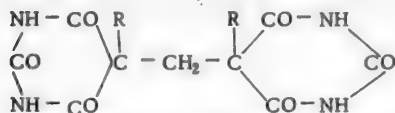
The constants, yields and analytical data of the methylene-bis-5-alkylbarbituric acids and of methylene-bis-barbituric acid itself are set forth in Table 2 (see following page).

SUMMARY

1. The alkylation of methylene-bis-malonic ester with sodium ethoxide and alkyl halides was investigated.
2. It was established that when employing in this reaction primary halides of normal structure, the yield of methylene-bis-alkylmalonic esters reached 40% of the theoretical, whereas when employing secondary halides or primary halides of branched structure the methylene-bis-alkylmalonic esters are not formed at all.
3. It was shown that the alkylation of methylene-bis-sodium malonic ester is accompanied by a secondary reaction involving cleavage, under the action of sodium ethoxide, of the intermediately formed sodium derivative of the monoalkylmethylene-bis-malonic ester; the products of this reaction are methylenemalonic ester (further transformed into a crystalline polymer) and monoalkylmalonic esters (yield from 11 to 40% when using primary halides of normal structure and 58-64% when using secondary bromides or primary ones with a branched structure).
4. Reaction of urea in presence of sodium ethoxide with the respective methylene-bis-alkylmalonic esters

TABLE 2

Methylene-bis-5-alkylbarbituric acids



Preparation number	R	Melting point	Yield (in % of theoretical)	N (in %)	
				Found	Calculated
1	H*	Decomposes without melting at about 300°	45.0	20.73 20.56	20.41
2	CH ₃	252-253	44.8	18.40 18.50	18.9
3	C ₂ H ₅	364-365 (with decomp.)	6.17	17.36 17.39	17.29
4	C ₃ H ₇	358-359 (with decomp.)	56.2	15.83 15.77	15.89
5	C ₄ H ₉	235-238	25.4	14.17 14.42	14.07
6	C ₆ H ₅ CH ₂	210-211	15.3	12.37 12.78	12.49

* Gisling and Schwarzenbach [1] described the preparation of methylene-bis-barbituric acid (R = H) but did not give analytical data.

gave the previously undescribed methylene-bis-5-alkylbarbituric acids (alkyl = methyl, ethyl, propyl and butyl; the benzyl radical can also be introduced in the same way)

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Received February 8, 1954

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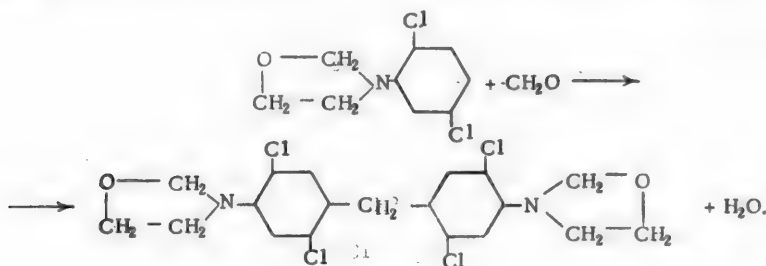


THE REACTION OF N-(2,5-DICHLOROPHENYL)-OXAZOLIDINE WITH FORMALDEHYDE

K. D. Petrov, E. S. Lagucheva and V. I. Pukhova

We have previously shown that 2,5-dichloroaniline, in contrast to aniline, does not react with ethylene oxide [1]. The apparent explanation of this difference in behavior is that the basic properties of 2,5-dichloroaniline are greatly weakened by the presence of a chlorine atom in the benzene ring, so that the amino group becomes non-reactive toward ethylene oxide.

In this connection it was of interest to establish whether the chlorine atoms in N-(2,5-dichlorophenyl)-oxazolidine which reacts with halogen-free N-phenyloxazolidine to form 4,4'-di-(oxazolidyl-N)-diphenylmethane, will react with formaldehyde. It should be noted that N-phenyloxazolidine reacts with formaldehyde with facility both in presence of hydrochloric acid [2] and of formic acid (experiment 2). It was found, however, that N-(2,5-dichlorophenyl)-oxazolidine does not react at all with formaldehyde in presence of formic acid, whereas in presence of hydrochloric acid condensation with formaldehyde takes place to give 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane according to the scheme.



The structure of the product is confirmed by the determination of the nitrogen content and by the previous observation [2] that this type of condensation proceeds in the para-position. In this connection it should be emphasized that the above reaction scheme is not inconsistent with the generally accepted rule of substitution in the aromatic nucleus [3]. This is also supported by the fact that in the present instance reaction in the para-position is easier than in, say, the ortho-position since in the former position of the molecule of N-(2,5-dichlorophenyl)-oxazolidine there are no considerable steric barriers (remoteness of the oxazolidine ring from the para-position) which might have hindered the formation of 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane. Moreover, reaction of dialkylanilines usually proceed in the para-position [3].

EXPERIMENTAL

1. 4,4'-Di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane. 54.5 g (0.25 mole) N-(2,5-dichlorophenyl)-oxazolidine, 12.3 g 36.7% formaldehyde (0.15 mole CH₂O), 70 ml alcohol and 1 ml hydrochloric acid (d 1.18) were stirred for 8 hours at room temperature. Heat was liberated at the start of the reaction and the temperature of the mass rose to 29°. At the conclusion of the stirring, the reaction mass was left overnight and the next day it was neutralized with sodium carbonate solution, when a white crystalline precipitate of 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane came down. The precipitate was filtered on a nutsch and washed with 80 ml alcohol and 250 ml water. The product was dried in the air. Yield 21 g (37.5%). After two recrystallizations from benzene, 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane melted at 154°.

0.3320, 0.4263 g sub.: 15.14, 19.02 ml 0.1 N H₂SO₄. Found %: N 6.38, 6.24. C₁₉H₁₆O₂N₂Cl₄. Calculated %: N 6.25.

2. Preparation of 4,4'-di-(oxazolidyl-N)-diphenylmethane in presence of formic acid. 14.9 g N-Phenyloxazolidine, 4.9 g formaldehyde solution, 50 ml alcohol and 2 ml 70% formic acid were heated to 35-35° and stirred 8 hours. During the operation 4,4'-di-(oxazolidyl-N)-diphenylmethane gradually came down in the form of white scales. At the conclusion of the stirring the reaction mixture was left overnight. The next day the mixture was neutralized with sodium carbonate solution. The crystals of 4,4'-di-(oxazolidyl-N)-diphenylmethane were collected on a nutsch, washed with 50 ml alcohol, then with 500 ml water and finally with another 30 ml alcohol. The air-dried product melted at 138-140°.

Yield 10.3 g (66.5%). After recrystallization from benzene the m.p. was 141-142° in agreement with that reported in the literature for 4,4'-di-(oxazolidyl-N)-diphenylmethane [2].

SUMMARY

It was shown that N-(2,5-dichlorophenyl)-oxazolidine reacts with formaldehyde in presence of hydrochloric acid with formation of 4,4'-di-(oxazolidyl-N)-2,2',5,5'-tetrachlorodiphenylmethane. It was also established that in presence of formic acid N-(2,5-dichlorophenyl)-oxazolidine does not enter into reaction with formaldehyde, whereas the halogen-free N-phenyloxazolidine condenses with formaldehyde in presence of formic acid to give 4,4'-di-(oxazolidyl-N)-diphenylmethane.

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Received February 5, 1954

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* T.p. = C. B. translation pagination.

ISOMERIZATION OF BICYCLIC TERPENE OXIDES DURING REACTION WITH ACETIC ANHYDRIDE

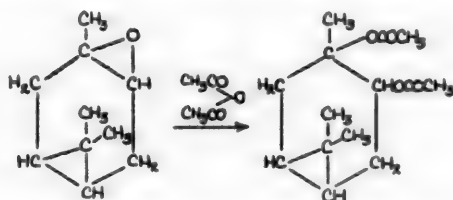
B. A. Arbuzov and Z. G. Isaeva

Researches by B. A. Arbuzov have established [1] that oxides of bicyclic terpene hydrocarbons – α -pinene, Δ^3 -carene, β -pinene and camphene – undergo isomerization in various reactions. In the Grignard and Reformatsky reactions the oxides undergo preliminary isomerization to aldehydes; α -pinene oxide isomerizes to campholenaldehyde, β -pinene oxide to dihydromyrtanal, camphene oxide to camphenilaldehyde, and Δ^3 -carene oxide to an unsaturated aldehyde of uncertain structure. Isomerization of some of these oxides (oxides of α -pinene and Δ^3 -carene) is accompanied by profound changes in their carbon skeleton. It was shown that the isomerizing agents during the Grignard and Reformatsky reactions are halides of magnesium and zinc.

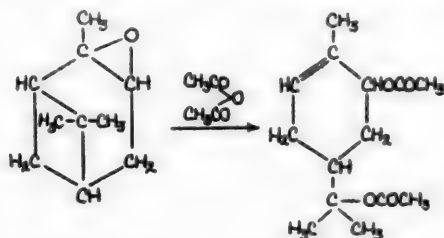
In 1949 we found [2] that the reaction of oxides of α -pinene, Δ^3 -carene and camphene with alcohols in presence of sulfuric acid is likewise accompanied by isomerization of the oxides to aldehydes. The aldehydes react with the alcohols in presence of the sulfuric acid to form acetals. The action of alcohols on α -pinene oxide gives, apart from acetals, monoesters of sobrerol.

With the objective of studying the behavior of oxides of bicyclic terpene hydrocarbons in reactions without catalysts, we undertook an investigation of the action of acetic anhydride on the oxides of α -pinene, Δ^3 -carene and camphene.

It was natural to assume that the reaction of oxides of α -pinene, Δ^3 -carene and camphene with acetic anhydride would proceed in such a way that the molecule of acetic anhydride would combine with the oxide ring to form acetates of the corresponding diols: pinene glycol, carene glycol and camphene glycol. For example, with Δ^3 -carene oxide:



Due to the circumstance, as reported in the literature, that α -pinene can isomerize even under mild conditions, its reaction with acetic anhydride might be expected to lead to sobrerol acetate (by analogy with the formation of sobrerol by the action of water on α -pinene oxide in presence of carbon dioxide [3]):



The experiments showed that the reaction of terpene bicyclic oxides with acetic anhydride is a complex process with formation of a mixture of products.

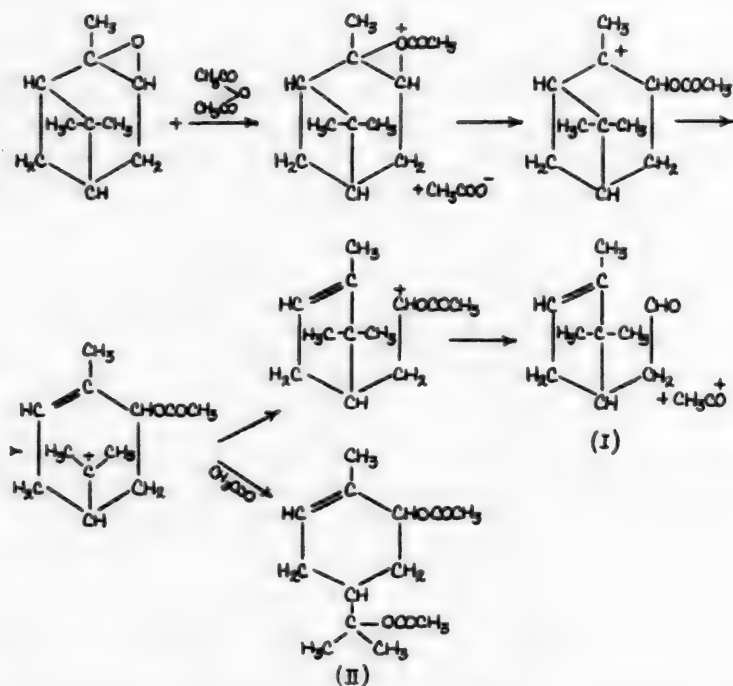
α -Pinene oxide

Three substances were isolated after reaction of α -pinene oxide with acetic anhydride. The constants of one of these substances with b.p. 58–64° (4 mm) were very similar to those campholenaldehyde (I) (see experimental). It was identified by preparation of the semicarbazone with m.p. 137–138°. The yield of campholenaldehyde in the reaction of α -pinene oxide with acetic anhydride was 20.4%.

The second reaction product with the composition $C_{12}H_{18}O_2$ (yield 30.2%) has b.p. 89-95° (6 mm). The compound gives an adduct with maleic anhydride with m.p. 142-144°. Hydrolysis of this compound with alkali in aqueous-alcoholic solution gave an alcohol with the composition $C_{10}H_{16}O$ and b.p. 75-81° (2.5 mm). The alcohol is esterified by boric acid; consequently, the hydroxyl group is not at the tertiary carbon atom. The compound $C_{12}H_{18}O_2$ is probably the acetate of the alcohol $C_{10}H_{16}O$ with conjugated double bonds. Its structure was not established.

The third reaction product is sobrerol diacetate (II): b.p. 125-128° (4 mm). Saponification of sobrerol acetate with 6% aqueous alkali solution gave sobrerol with m.p. 149-150°. There was no melting point depression in a mixed test with sobrerol prepared by hydration of α -pinene oxide in presence of acid. Yield of sobrerol acetate 26.1%.

In previous papers dealing with the rearrangements taking place on reaction of oxides of bicyclic terpenes with various reactants, we made use of a scheme in which was assumed the formation at an intermediate stage of an oxonium ion which later rearranged to a carbonium ion. Rearrangements of the carbonium ion would readily account for the formation of diverse products of reaction. Similar concepts explain the formation of the products of reaction with acetic anhydride of the oxide of α -pinene and, as will be shown later, of oxides of other bicyclic terpenes. Formation of the products of reaction of α -pinene oxide with acetic anhydride may be represented by the following scheme:

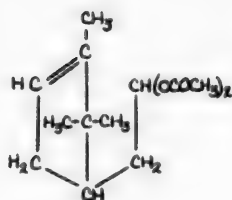


With the objective of elucidating the role of campholenaldehyde in the reaction of α -pinene oxide with acetic anhydride and, in particular, in the formation of the compound $C_{12}H_{18}O_2$, an experiment was performed on the action of acetic anhydride on campholenaldehyde under the reaction conditions (heating at 140° without a catalyst). Campholenaldehyde is unchanged under these conditions.

Reaction of acetic anhydride with campholenaldehyde in presence of sulfuric acid gave a crystalline substance with m.p. 70-72° whose analysis corresponded to $C_{14}H_{22}O_4$. Saponification of the compound with an aqueous-alcoholic solution of alkali gave campholenaldehyde (m.p. of semicarbazone 137-138°). Consequently, the compound with m.p. 70-72° is the diacetate with structure (III).

Δ^3 -Carene Oxide

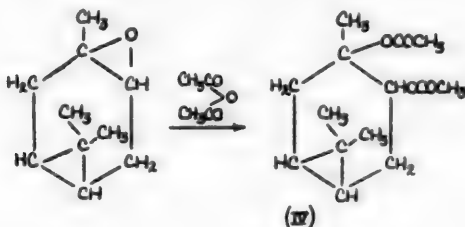
Δ^3 -Carene oxide gives two products in reaction with acetic anhydride. 58.6 % of the carene oxide entered into the reaction, the remainder being recovered unchanged. As in the case of α -pinene oxide, a compound



(III)

$C_{12}H_{18}O_2$ with b.p. 86-88.5° (3 mm) was isolated. Yield 21.6%. This compound gives an adduct with maleic anhydride with m.p. 145-147°. A mixed test with the adduct of the analogous compound obtained by reaction of α -pinene oxide with acetic anhydride showed a depression, the mixed melting point being 117-120°. Saponification of the compound $C_{12}H_{18}O_2$ gives an alcohol $C_{10}H_{16}O$. As in the case of the product of reaction of α -pinene oxide with acetic anhydride, the structure of the compound $C_{12}H_{18}O_2$ was not established.

The second product of reaction of Δ^3 -carene oxide with acetic anhydride was β -carene glycol diacetate (IV) with b.p. 120-121° (4 mm). Yield 7.7%. Saponification of this product gave β -carene glycol with m.p. 88-89°. Consequently, the reaction of Δ^3 -carene with acetic anhydride proceeds partially with isomerization of Δ^3 -carene oxide and in part normally.



Camphene Oxide

The reaction of camphene oxide with acetic anhydride proceeds with complete isomerization of the oxide. In this process 38.3% of the camphene oxide isomerizes to camphenilanic aldehyde (V) which was identified by preparation of the semicarbazone with m.p. 191-192°. Among the reaction products was also found the compound $C_{12}H_{18}O_2$ with b.p. 93-95.5° (5 mm), n_D^{20} 1.4850, d_4^{20} 1.0043. Yield 20%. An aqueous-alcoholic solution of alkali saponifies the compound to camphenilanaldehyde. These data indicate that the compound is the acetate of the enolic form of camphenilanic aldehyde (VI).

The acetate of the enolic form of camphenilanic aldehyde was prepared by Semmler in 1909 [4] by the action of acetic anhydride and sodium acetate on camphenilanaldehyde. Semmler gave the following constants for the acetate of the enolic form of camphenilanaldehyde: b.p. 113-116° (10 mm), d_4^{20} 1.0125, n_D^{20} 1.4816.

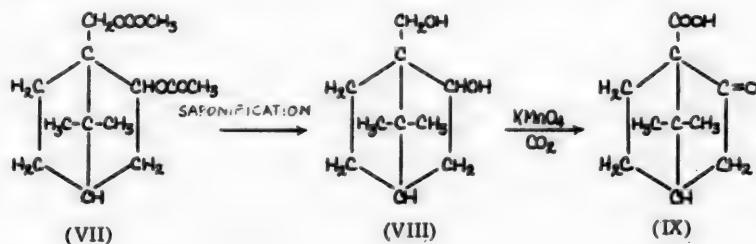
The third reaction product was a compound $C_{14}H_{22}O_4$ (VII) with b.p. 128-130° (5 mm). Yield 20.4%.

By analogy with the compounds of the same composition obtained from the oxides of α -pinene and Δ^3 -carene it may be suggested that the action of acetic anhydride on camphene oxide also gives the acetate of a diol. Saponification with alkali gave a crystalline substance with m.p. 241-243° (VIII).

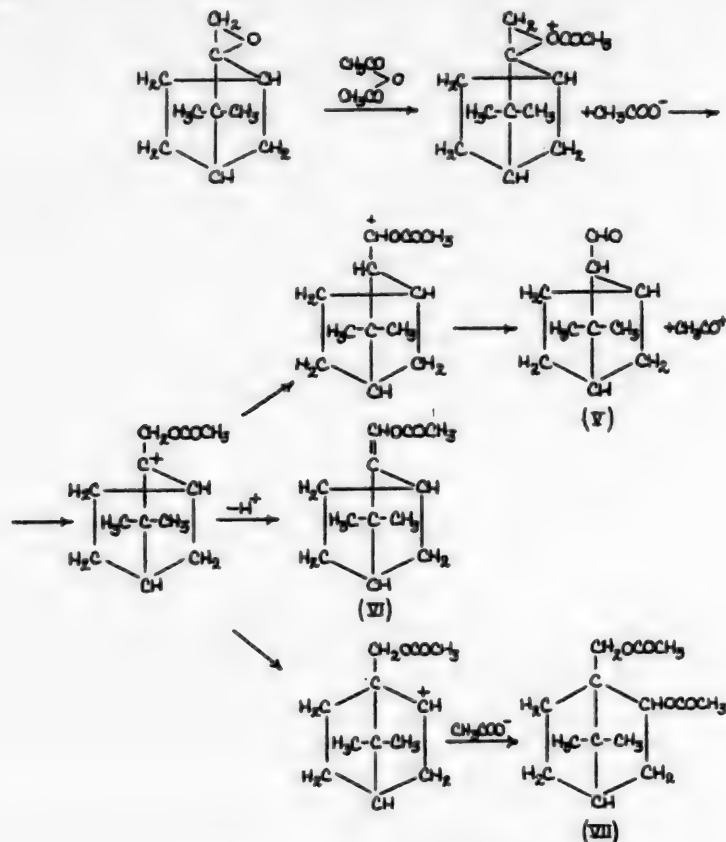
The crystalline compound was oxidized with potassium permanganate in a stream of carbon dioxide to form ketopininc acid with m.p. 232-233° (IX).

For confirmation of the identity of the product of oxidation of the diol with m.p. 241-243°, ketopininc acid with m.p. 230-232° was prepared, as described in the literature [5] by oxidation of bornyl chloride with nitric acid. A mixed test did not give a melting point depression.

Consequently, the product with b.p. 128-130° (5 mm) must be assigned the structure of the diacetate of 2,10-camphanediol (VII).



The mechanism of the reaction of camphene oxide with acetic anhydride may be represented by the following scheme:



EXPERIMENTAL

Action of acetic anhydride on α -pinene oxide

α -Pinene oxide was prepared by oxidation of α -pinene with peracetic acid; it had the constants: b.p. 67-67.5° (12 mm), d_4^{20} 0.9601, n_D^{20} 1.4693.

1st experiment. Reactants were 96.8 g pinene oxide and 151 g acetic anhydride. The α -pinene oxide was run dropwise into the boiling acetic anhydride in the course of 1½ hours. Then the reaction mixture was boiled 4½ hours (temperature in the reaction mixture 140-143°). The acetic anhydride was distilled off in vacuum; fractionation of the residue in a Widmer column yielded three fractions:

1st - b.p. 58-64° (4 mm), 19.7 g, d_4^{20} 0.9172, n_D^{20} 1.4650; 2nd - b.p. 89-95° (6 mm), 29.9 g, d_4^{20} 0.9759, n_D^{20} 1.4802; 3rd - b.p. 125-128° (4 mm), 33.6 g, d_4^{20} 1.0456, n_D^{20} 1.4668.

2nd experiment. Reactants were 86.5 g α -pinene oxide and 257 g acetic anhydride. The α -pinene oxide was run into the acetic anhydride, heated to 130°, in the course of 45 minutes. After running in ¼ of the amount of α -pinene oxide, the reaction mixture boiled. After all had been run in, the reaction mixture was boiled for another 40 minutes. The mixture was worked up as described for the 1st experiment, and also gave three fractions:

1st - b.p. 66-71° (5 mm), 22.2 g, d_4^{20} 0.9187, n_D^{20} 1.4668; 2nd - b.p. 94-100° (4.5 mm), 20.9 g, d_4^{20} 0.9756, n_D^{20} 1.4805; 3rd - b.p. 134-136° (4 mm), 29 g, d_4^{20} 1.0462, n_D^{20} 1.4685.

Preparation of the semicarbazone of campholenaldehyde. Semicarbazide hydrochloride (1.1 g) and sodium acetate (1.5 g) were dissolved in a little water and into the solution was run the compound (1.1 g) with b.p. 58-64° (4 mm). Shaking of the mixture for 20-25 minutes resulted in separation of a solid; weight 1.3 g after washing with water and pressing on filter paper. After two recrystallizations from ethyl alcohol the m.p. of the semicarbazone was 137-138°. The m.p. of campholenaldehyde semicarbazone was 138-139°. The mixed melting point was 137-138°.

Examination of substance with b.p. 89-95° (6 mm)

d_4^{20} 0.9759, n_D^{20} 1.4802, MR_D 56.49. $C_{12}H_{18}O_2F_2$. Calculated 56.14.

0.0966, 0.1000 g substance: 0.2602, 0.2692 g CO_2 ; 0.0778, 0.0808 g H_2O . Found %: C 73.45, 73.42; H 8.95, 8.97. $C_{12}H_{18}O_2$. Calculated %: C 74.18; H 9.35.

Preparation of the adduct of the substance with b.p. 89-95° (6 mm) with maleic anhydride. A mixture of 3 g substance and 1.6 g maleic anhydride was heated on a water bath at 80-85° for 6 hours. The small precipitate which came down on cooling was filtered off. Crystals came down from the filtrate on standing; m.p. 142-144° after three recrystallizations from alcohol. The adduct is readily soluble in alcohol.

Saponification of substance with b.p. 89-95° (6 mm) with aqueous-alcoholic NaOH. Into a solution of 1.7 g NaOH in 11 ml water and 21 ml alcohol was run 8 g substance. The color of the mixture became light-brown. The color changed to reddish-brown on heating at 40-45° for 5 hours. The reaction mixture was then diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after driving off the ether and alcohol was vacuum-distilled:

b.p. 75-81° (2.5 mm), 4.5 g, d_4^{20} 0.9648, n_D^{20} 1.5010, MR_D 46.41. $C_{10}H_{16}OF_2$. Calculated 46.77.

0.0880 g substance: 0.2542 g CO_2 ; 0.0818 g H_2O . 0.1116 g substance: 16.8 ml CH_4 (14°, 758 mm). Found %: C 78.78; H 10.32; OH 10.88. $C_{10}H_{16}O$. Calculated %: C 78.89; H 10.59; OH 11.18.

Action of acetic anhydride on campholenaldehyde in presence of sulfuric acid

Reactants were 10 g campholenaldehyde [b.p. 76-82° (9 mm), d_4^{20} 0.9215, n_D^{20} 1.4650], 35 g freshly distilled acetic anhydride and 1 drop sulfuric acid (d 1.84). The campholenaldehyde was run dropwise into the acetic anhydride containing the sulfuric acid. No heating of the mixture was detected. The reaction mixture was heated on a water bath at 65° for 1 hour and then neutralized with sodium acetate. The residue after removal of the acetic anhydride was distilled in vacuum in a Widmer column to give three fractions:

1st - b.p. 75-80° (3 mm), 2 g, n_D^{20} 1.4730; 2nd - b.p. 80-90° (3 mm), 1.7 g, d_4^{20} 0.9870, n_D^{20} 1.4672; 3rd - b.p. 90-120° (3 mm), 3.3 g, n_D^{20} 1.4697.

The 2nd and 3rd fractions at once started to crystallize. The crystals were filtered off, and pressed on filter paper; weight 3.2 g. After 3 recrystallizations from alcohol the m.p. was 70-72°.

0.1240 g substance: 0.2990 g CO_2 ; 0.0972 g H_2O . Found %: C 65.76; H 8.71. $C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.72.

Saponification of substance with m.p. 70-72°. 1 g substance was treated with 0.5 g NaOH in 10 ml water and 10 ml ethanol. The mixture was heated on a water bath at 90-100° for 6 hours. The reaction mixture was diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The ether was distilled off; from the residue was obtained campholenaldehyde semicarbazone with m.p. 137-138°.

Examination of substance with b.p. 125-128° (4 mm)

d_4^{20} 1.0456, n_D^{20} 1.4668, MR_D 67.38. $C_{14}H_{22}O_4$. Calculated 67.49.

0.1332 g substance: 0.3214 g CO_2 ; 0.1030 g H_2O . Found %: C 65.81; H 8.58. $C_{14}H_{22}O_4$. Calculated %: C 66.1; H 8.72.

Saponification of substance with b.p. 125-128° (4 mm). A mixture of 4 g substance, 2 g NaOH and 32 ml water was shaken at room temperature for 70 hours. The precipitated crystals were filtered and washed with ether. M.p. 147-149°. After recrystallization from alcohol the m.p. was 149-150° (sobrerol has m.p. 150°). A mixed test with the sobrerol prepared by hydration of α -pinene oxide in presence of acid melted at 148-150°.

Action of acetic anhydride on Δ^3 -carene oxide

Reactants were 70 g Δ^3 -carene oxide [b.p. 72-74° (10.5 mm) d_4^{20} 0.9475, n_D^{20} 1.4680] and 190 g freshly distilled acetic anhydride. The Δ^3 -carene oxide was run into the boiling acetic anhydride in the course of 2 hours 40 minutes; the solution was then boiled for another 4 hours. Three fractions were collected on fractionation of the mixture:

1st - b.p. 51-54 (4 mm), 29 g, d_4^{20} 0.9480; n_D^{20} 1.4690; 2nd - b.p. 86-88.5° (3 mm), 11.3 g, d_4^{20} 0.9802, n_D^{20} 1.4790; 3rd - b.p. 120-121° (4 mm), 5.3 g, d_4^{20} 1.0455, n_D^{20} 1.4670.

Examination of substance with b.p. 86-88.5° (3 mm)

d_4^{20} 0.9802, n_D^{20} 1.4790, MR_D 56.12. $C_{12}H_{18}O_2$. Calculated 56.14.

0.1196 g sub.: 0.3252 g CO_2 ; 0.1000 g H_2O . Found %: C 74.15; H 9.29, $C_{12}H_{18}O_2$. Calc. %: C 74.18; H 9.35.

Preparation of adduct with b.p. 86-88.5° (3 mm) with maleic anhydride. A mixture of 2.9 g substance and 1.6 g maleic anhydride was heated on a water bath at 50° until the maleic anhydride had dissolved. On standing, crystals came down which were filtered off, washed with ether, and recrystallized from alcohol; m.p. 145-146°. The melting point after boiling with ligroine was 145-147°.

Saponification of substance with b.p. 86-88.5° (3 mm). Reactants were 4.5 g substance and 1.8 g KOH in 8 ml water and 15 ml ethanol. On mixing the reactants a dark-brown color was imparted to the mixture and a still darker color was acquired after heating on a water bath at 40-45° for 5 hours. The mixture was then diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after driving off the ether and alcohol was distilled to give 1.9 g substance with b.p. 75.5-77° (2.5 mm).

d_4^{20} 0.9636, n_D^{20} 1.4964, MR_D 46.12. $C_{10}H_{16}O_2$. Calculated 46.77.

0.1283 g sub.: 20.61 ml CH_4 (20°, 760 mm). Found %: OH 11.39. $C_{10}H_{16}O$. Calculated %: OH 11.18.

Examination of substance with b.p. 120-121° (4 mm)

d_4^{20} 1.0455, n_D^{20} 1.4670, MR_D 67.41. $C_{14}H_{22}O$. Calculated 66.46.

0.0930 g sub.: 0.2260 g CO_2 ; 0.0716 g H_2O . Found %: C 66.27; H 8.55 $C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.72.

Saponification of substance with b.p. 120-121° (4 mm). A mixture of 1.5 g substance, 1.2 g NaOH and 19 ml water was shaken 17 hours at room temperature. The resultant crystals were filtered off, washed with ether and recrystallized three times from ligroine; m.p. 88-89°. Melting point of anhydrous β -carene glycol 89-90°. A mixed test with β -carene glycol prepared by hydration of Δ^3 -carene oxide in presence of hydrochloric acid (m.p. after two two recrystallizations from ligroine 88-89°) gave a melting point of 87-89°.

Action of acetic anhydride on camphene oxide

Reactants were 50.4 g camphene oxide and 136 g acetic anhydride. The solution of camphene oxide in acetic anhydride was heated on a water bath for 3 hours and then boiled for 7 hours. Repeated fractionations of the reaction mixture in a Widmer column gave three fractions.

1st - b.p. 80-87° (9.5 mm) 19.3 g (crystallizes on distillation); 2nd b.p. 93-95.5° (5 mm) 7.9 g d_4^{20} 1.0043, n_D^{20} 1.4850; 3rd b.p. 128-130° (5 mm), 10.6 g, d_4^{20} 1.072, n_D^{20} 1.4718.

Preparation of semicarbazone of camphenilanaldehyde

To a saturated solution of 1 g semicarbazide hydrochloride and 1.5 g sodium acetate in water was added 1 g substance with b.p. 80.87° (9.5 mm). The mixture was diluted with methanol until the substance dissolved. On shaking for 2-3 minutes the solution deposited a white precipitate which was filtered off, washed with water and pressed on filter paper. Recrystallization from ethanol gave fine crystals with m.p. 191-192°. No change of m.p. after a second recrystallization. The semicarbazone of the camphenilanaldehyde prepared by isomerization of camphene oxide with zinc bromide had m.p. 191-192° [1]. A mixed sample melted at 190-192°.

Examination of substance with b.p. 93-95.5° (5 mm).

d_4^{20} 1.0043, n_D^{20} 1.4850, MR_D 55.36 $C_{12}H_{18}O_2$. Calculated 55.0.

0.1254 g sub.: 0.3412 g CO_2 ; 0.1022 g H_2O . Found %: C 74.20; H 9.06. $C_{12}H_{18}O_2$. Calculated %: C 74.18. H 9.35.

Saponification of substance with b.p. 93-95.5° (5 mm). A mixture of 4.1 g substance, 1.3 g KOH, 6 ml water and 14 ml ethanol was heated on a water bath for 12 hours at 80-85°, after which it was diluted with water and extracted with ether. The ethereal extract was dried with sodium sulfate. The residue after removal of the ether and alcohol was distilled to give a fraction with:

B.p. 65-72° (3 mm) 1.6 g, d_4^{20} 1.0087, n_D^{20} 1.4848.

Crystallization commenced even during distillation. The crystals were filtered off and pressed on filter paper; a semicarbazone was prepared from them.

Preparation of semicarbazone of camphenilanaldehyde. Reactants were 0.2 g substance, 0.3 g semicarbazide and 0.4 g sodium acetate. To the mixture was added methanol until the aldehyde dissolved. On shaking, a precipitate came down; weight of crude semicarbazone 0.1 g. M.p. 189-190° after two recrystallizations from alcohol. A mixture with the semicarbazone of camphenilanaldehyde prepared by isomerization of camphene oxide in the reaction with acetic anhydride melted at 189-190°.

Examination of substance with b.p. 128-130° (5 mm)

d_4^{20} 1.072, n_D^{20} 1.4718, MR_D 66.33. $C_{14}H_{22}O_4$. Calculated 65.76.

0.0950 g sub.: 0.2298 g CO_2 ; 0.0732 g H_2O . Found %: C 65.97; H 8.56. $C_{14}H_{22}O_4$. Calculated %: 66.11; H 8.72.

Saponification of substance with b.p. 128-130° (5 mm). 6 g substance was treated with 2.5 g NaOH in 15 ml water and 15 ml alcohol. The mixture was heated on a water bath 8 hours at 40-50°. The reaction mixture was diluted with water and extracted with ether. The residue after removal of the ether became viscous but did not crystallize. On dilution with ligroine a crystalline product separated. Recrystallization from ligroine gave 1.2 g substance with m.p. 238-242°; after recrystallization the m.p. was 241-243°. The melting point was unchanged after a third recrystallization.

0.0578 g sub.: 0.1493 g CO_2 ; 0.0560 g H_2O . Found %: C 70.45; H 10.76. $C_{10}H_{18}O_2$. Calculated %: C 70.54 H 10.65.

Oxidation of substance with m.p. 241-243°. 1.2 g substance was dissolved in 120 ml water with heating. To the solution, cooled to 20°, was added with stirring a solution of 2.4 g $KMnO_4$ in 60 ml water. Oxidation was effected in a stream of carbon dioxide. After two days' standing the reaction mixture was steam-distilled and 250 ml solution came over and was extracted with ether prior to evaporation. After concentration to a volume of 10 ml, the solution was acidified with hydrochloric acid and extracted with ether. The residue after removal of the ether crystallized completely on standing. After two recrystallizations from ligroine the m.p. was 232-233°.

Oxidation of bornyl chloride with nitric acid. 13 g bornyl chloride was treated with 23.9 g 94% nitric acid. The bornyl chloride was introduced into the nitric acid in small portions while cooling with water. Reaction was conducted at a temperature not higher than 24°. After standing at room temperature for 30 hours, the reaction mixture was neutralized with milk of lime and the solution filtered. The filtrate was saturated with carbon dioxide and again filtered before evaporation to a small volume; it was then acidified with hydrochloric acid and extracted with ether. After removal of the ether, the residue crystallized; weight 1.8 g. M. p. 230-232° after recrystallization from water. A mixture with the acid prepared by oxidation of the diol with m.p. 241-243° melted at 230-232.5°.

SUMMARY

1. A study was made of the reaction of α -pinene oxide, Δ^3 -carene oxide and camphene oxide with acetic anhydride.
2. In this reaction α -pinene oxide yielded campholenaldehyde, sobrerol diacetate and the acetate of a dienic alcohol of unclarified structure.
3. Reaction of Δ^3 -carene oxide with acetic anhydride gave β -carene glycol diacetate and the acetate of a dienic alcohol of unknown structure.
4. Camphene oxide with acetic anhydride forms camphenilanaldehyde, the acetate of the enolic form of camphenilanaldehyde and 2,10-camphanediol acetate.
5. A mechanism is advanced for the formation of diverse reaction products which assumes rearrangement to the carbonium ion.

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Received February 22, 1954

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* T.p. = Consultants Bureau Translation pagination.



SYNTHESIS OF ORGANOANTIMONY COMPOUNDS OF THE TYPE OF Ar_2SbX_3 and Ar_3SbX_2 VIA THE DOUBLE DIAZONIUM SALTS OF ANTIMONY PENTACHLORIDE

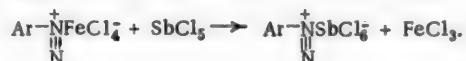
O. A. Reutov and V. V. Kondratyeva

Double diazonium salts of antimony trichloride (May salts), prepared more than 40 years ago [1], have found wide application for synthesis of diverse aromatic organoantimony compounds. Unlike the May salts, the double diazonium salts of antimony pentachloride were entirely unknown, since their preparation even in a strongly acidic aqueous medium is hindered by the facility of hydrolysis of SbCl_5 , and the employment of organic hydroxyl-free solvents is prevented by the poor solubility in the latter of aryl diazonium chlorides.

Their synthesis has been effected by utilizing the exchange reaction (discovered by one of us [2]) between double diazonium salts of ferric chloride and chlorides of other heavy metals:



On running a solution of antimony pentachloride in chloroform or carbon tetrachloride into an acetone solution of $\text{ArN}_2\text{Cl} \cdot \text{FeCl}_3$ and then stirring in ether, the double diazonium salt of antimony pentachloride comes down:



The double salts synthesized by this reaction are set forth in Table 1.

The double diazonium salts of antimony pentachloride proved to be a convenient starting point for synthesis of organoantimony compounds of the type of Ar_2SbX_3 and Ar_3SbX_2 . Their decomposition by iron powder in an acetone medium proceeds according to two equations:



The results of decomposition of various double diazonium salts of antimony pentachloride by iron powder are set forth in Table 2.

As we see from the data of Table 2, only one of the above reactions takes place in most cases, and (usually in high yield) only one type of organoantimony compound is formed.

EXPERIMENTAL



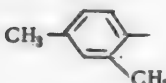
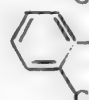
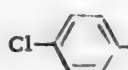

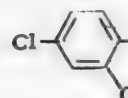
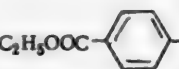
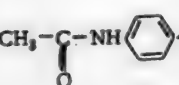
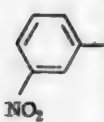
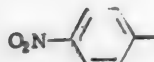
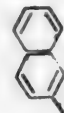
Preparation of double diazonium salts of ferric chloride. Preparation of the double salts of aryl diazonium chlorides ($\text{ArN}_2\text{Cl} \cdot \text{FeCl}_3$) was effected under the conditions described by Kocheshkov and Nesmeyanov [3] with a slight modification consisting in dissolving the ferric chloride in the minimum amount of water heated to 50-60°, after which the solution was cooled to -5°. The cooled solution of ferric chloride was run into a cooled solution of the diazotized amine, after which the double salt of aryl diazonium chloride and ferric chloride was precipitated by addition with stirring of concentrated hydrochloric acid. By this procedure intense cooling is not required. Precipitation of the double salt proceeds readily even at temperatures of 0 to +5°. The prepared salts can (if necessary) be purified by reprecipitation with ether from acetone solution. The pure, dry double salts of aryl diazonium chlorides and ferric chloride are fairly stable and they can be stored in the air for periods of 2-3 days to 2 weeks (depending upon the nature of the aromatic radical) without appreciable decomposition.

The following double diazonium salts were synthesized for the first time by the above-described procedure:

Double salt of ferric chloride and p-carbethoxyphenyl diazonium chloride ($\text{p-C}_6\text{H}_4\text{OOCCH}_2\text{N}_2\text{Cl} \cdot \text{FeCl}_3$) with m.p. 72-73° (decomp.), greyish-yellow color; yield 88%.

TABLE 2

Substances formed by decomposition of double diazonium salts of antimony pentachloride $\text{ArN}_2\text{Cl} \cdot \text{SbCl}_5$ by iron powder in acetone

Ar-	Ar ₂ SbX ₃						
	Formula	Yield (in %)	in the form of which compound it is identified	melting point	color	results	
						C	
						calcu- lated	found
	(C ₆ H ₅) ₂ SbOOH	67	(C ₆ H ₅) ₂ SbCl ₃	171-172°	white	31.06	31.42 31.36
	(CH ₃ C ₆ H ₄) ₂ SbOOH	58	(CH ₃ C ₆ H ₄) ₂ SbCl ₃	155	white	40.95	41.02 41.10
				Not formed			
				Not formed			
	(ClC ₆ H ₄) ₂ SbOOH	59	(ClC ₆ H ₄) ₂ SbCl ₃	149-150	white	31.92	31.68 31.83
	(IC ₆ H ₄) ₂ SbOOH	81	(IC ₆ H ₄) ₂ SbOCl*	149	white	—	—
				Not formed			
				Not formed			
				Not formed			
	(O ₂ NC ₆ H ₄) ₂ SbOOH	72	(O ₂ NC ₆ H ₄) ₂ SbCl ₃	182-185	white	30.50	30.37 30.43
	(O ₂ NC ₆ H ₄) ₂ SbOOH	88	(O ₂ NC ₆ H ₄) ₂ SbCl ₃	190 (contracts)	white	30.50	30.28 30.36
				Not formed			

* Substance described for first time.

				Ar ₃ SbX ₂									
of analysis (in %)				Formula	melting point	color	Yield (in %)	results of analysis (in %)					
H		Sb						C		H		Sb	
calcu- lated	found	calcu- lated	found					calcu- lated	found	calcu- lated	found	calcu- lated	found
2.61	2.83 2.92	-	-				Not formed						
3.44	3.21 3.43	-	-	(CH ₃ C ₆ H ₄) ₃ SbCl ₂	156°	white	29	-	-	-	-		
				[(CH ₃) ₂ C ₆ H ₃ I ₃]SbCl ₂	190.5- 191.5	white	52	56.71	57.03 57.01	5.39	5.48 5.55		
				(ClC ₆ H ₄) ₃ SbCl ₂	205- 206	white	73	40.97	40.91 40.82	2.30	2.25 2.18		
1.79	1.72 1.85	-	-	(ClC ₆ H ₄)SbCl ₂	193	white	30	40.97	41.05 40.97	2.30	2.36 2.55		
			21.03										
-	-	21.02	21.15				Not formed						
				(Cl ₂ C ₆ H ₃) ₃ SbCl ₂ •	235	white	60	-	-	-	19.00 19.20		
				(C ₂ H ₅ OOCC ₆ H ₄) ₃ SbCl ₂	133- 134	white	20	50.63	50.86 50.91	4.24	4.08 4.17		
				(CH ₃ CONHC ₆ H ₄) ₃ SbCl ₂	170 (sintering)	white	76	48.42	48.34 48.20	4.07	3.98 3.89		
1.71	1.52 1.67						Not formed						
1.71	1.78 1.64	-	-				Not formed						
				(C ₁₀ H ₇) ₃ SbCl ₂ •	158- 168	white	79	62.74	62.43 62.54	3.69	3.87 3.82		

TABLE 1

Double Diazonium Salts of Antimony Pentachloride.

Formula	M.p. (with decomp.)	Solubility			Color	Yield (in %)	Results of analysis (in %)						
		acetone	alcohol				ether benzene water.	C		H		N	
			Calcd.	Found				Calcd.	Found	Calcd.	Found	Calcd.	Found
							Calcd.	Found	Calcd.	Found	Calcd.	Found	
$C_6H_5N_2Cl \cdot SbCl_5$	66-67°	5	4	1	2	1	16.39	16.04	1.15	1.56	6.37	6.38	
	107-107.5	5	4	1	2	1	16.91	16.91	1.42	1.42	6.56	6.56	
$p\text{-}CH_3C_6H_4N_2Cl \cdot SbCl_5$							18.52	18.68	1.55	1.52	6.17	6.67	
							18.46	18.46	1.57	1.57	6.59	6.59	
$o\text{-}ClC_6H_4N_2Cl \cdot SbCl_5$	139	5	4	1	2	1	15.29	15.26	0.85	1.17	5.91	6.16	
							15.39	15.39	1.02	1.02	5.91	6.32	
$p\text{-}ClC_6H_4N_2Cl \cdot SbCl_5$	144	5	4	2	1	1	-	-	-	-	5.91	6.32	
							-	-	-	-	6.48	6.48	
$p\text{-}BrC_6H_4N_2Cl \cdot SbCl_5$	165-167	5	4	2	1	1	-	-	-	-	5.40	5.33	
							-	-	-	-	5.36	5.36	
$p\text{-}YC_6H_4N_2Cl \cdot SbCl_5$	123-124	5	4	1	1	1	-	-	-	-	4.95	4.81	
							-	-	-	-	4.65	4.65	
$2,4\text{-}Cl_2C_6H_3N_2Cl \cdot SbCl_5$	155	5	4	1	1	1	-	-	-	-	-	-	
							-	-	-	-	24.00	24.24	
$2,4,6\text{-}Br_3C_6H_2N_2Cl \cdot SbCl_5$	223	5	3	1	1	1	-	-	-	-	-	24.12	
							-	-	-	-	18.60	18.77	
$p\text{-}C_2H_5OOC C_6H_4N_2Cl \cdot SbCl_5$	104-105	5	2	1	1	1	-	-	-	-	-	18.72	
							-	-	-	-	23.80	23.90	
$p\text{-}(CH_3)_2NC_6H_4N_2Cl \cdot SbCl_5$	143	5	2	1	1	1	-	-	-	-	-	23.95	
							-	-	-	-	25.23	25.51	
$p\text{-}CH_3CONHC_6H_4N_2Cl \cdot SbCl_5$	143-145	5	3	1	1	1	-	-	-	-	-	25.32	
							-	-	-	-	29.67	29.98	
$o\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_5$	149-150	5	4	1	2	1	-	-	-	-	8.67	8.98	
							-	-	-	-	8.78	8.78	
$m\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_5$	141-142	5	4	1	2	1	-	-	-	-	8.67	8.50	
							-	-	-	-	8.78	8.78	
$p\text{-}O_2NC_6H_4N_2Cl \cdot SbCl_5$	114-115	5	4	1	2	1	-	-	-	-	8.67	8.57	
							-	-	-	-	8.63	8.63	
$\alpha\text{-}C_{10}H_7N_2Cl \cdot SbCl_5$	77-78	4	3	1	1	1	-	-	-	-	5.72	5.82	
							-	-	-	-	5.77	5.77	
$\beta\text{-}C_{10}H_7N_2Cl \cdot SbCl_5$	92	4	3	1	1	1	24.51	24.56	1.44	1.58	5.72	5.90	
$2,4\text{-}(CH_3)_2C_6H_3N_2Cl \cdot SbCl_5$	78-78.5	5	2	1	1	1	-	-	-	1.50	5.84	5.84	
							-	-	-	-	5.99	6.34	
$p\text{-}p'\text{-}Cl_3Sb \cdot ClN_2C_6H_4\text{-}C_6H_4N_2Cl \cdot SbCl_5$	125-126	4	3	1	1	2	-	-	-	-	6.38	6.42	
							-	-	-	-	6.72	6.72	
							-	-	-	-	6.60	6.60	

Double salt of ferric chloride and p-dimethylaminophenyldiazonium chloride [$p-(CH_3)_2NC_6H_4N_2Cl \cdot FeCl_3$] with m.p. 109° (decomp.), yellow color; yield 87%.

Double salt of ferric chloride and p-acetylaminophenyldiazonium chloride [$p-CH_3CONHC_6H_4N_2Cl \cdot FeCl_3$] with m.p. 109° (decomp.), yellow color; yield 80%.

Double salt of ferric chloride and m-xylyldiazonium chloride [$2,4-(CH_3)_2C_6H_3N_2Cl \cdot FeCl_3$] with m.p. 45-46° (decomp.), light yellow-color; yield 80%.

Double salt of ferric chloride and 2,4-dichlorophenyldiazonium chloride [$2,4-Cl_2C_6H_3N_2Cl \cdot FeCl_3$] with m.p. 132° (decomp.), light yellow color; yield 89%.

Double salt of ferric chloride and 2,4,6-tribromophenyldiazonium chloride [$2,4,6-Br_3C_6H_2N_2Cl \cdot FeCl_3$] with m.p. 126° (decomp.), yellow color; yield 63%.

Double salt of ferric chloride and α -naphthyldiazonium chloride [$\alpha-C_{10}H_7N_2Cl \cdot FeCl_3$] with m.p. 75-77° yellow color; yield 73%.

Double salt of ferric chloride and β -naphthyldiazonium chloride [$\beta-C_{10}H_7N_2Cl \cdot FeCl_3$] with m.p. 78-79° (decomp.), yellow color; yield 87%.

Double salt of ferric chloride and diazotized benzidine [$p,p'-Cl_3Fe \cdot ClN_2C_6H_4-C_6H_4N_2Cl \cdot FeCl_3$], decomposes with explosion at 97-98°, yellow color, yield 86%.

Preparation of double diazonium salts of antimony pentachloride. 0.05 mole double salt of ferric chloride and aryl-diazonium chloride was dissolved in the cold in the minimum amount of dry acetone. To the solution was added (with cooling with snow and salt and with stirring) a solution 18 g (0.06 mole) antimony pentachloride in 75 ml cold, dry chloroform. To the resultant crystal magma with continued stirring was added 200 ml ether. The precipitate of double salt $ArN_2Cl \cdot SbCl_5$ was filtered off, washed with ether and dried in the air. The double diazonium salts of antimony pentachloride can be obtained in the analytically pure form by reprecipitation in the cold with ether from acetone solution. They can be stored in the air without appreciable decomposition for 1-2 weeks to 2-4 months depending upon the nature of the aromatic radical. The double diazonium salts of antimony pentachloride synthesized by this procedure are set forth in Table 1.

Decomposition of double diazonium salts of antimony pentachloride with iron powder. To a suspension of 5.6 g (0.1 g-atom) iron powder, passed through a 100-mesh screen, in 50 ml dry acetone was added a solution of 0.025 mole double salt of antimony pentachloride and aryldiazonium chloride in 40 ml dry acetone with good mechanical stirring in the course of 15 minutes. The first third of the solution was run in a single portion; 5 minutes later, when vigorous evolution of nitrogen had started and the reaction mixture had heated up, the remainder of the solution was run in at such rate that a continuous vigorous stream of gas was coming off. After the whole of the solution had been run in, the mixture was stirred for another 1/2 hour.

The inorganic precipitate was filtered off and the solvent distilled off from the filtrate in vacuum in the cold. To the residue (brown oil), after washing with 5 N hydrochloric acid (20 and 15 ml), was added 30 ml cold 96% alcohol with stirring. The insoluble triarylantimony dichloride was filtered off and recrystallized from a suitable solvent.

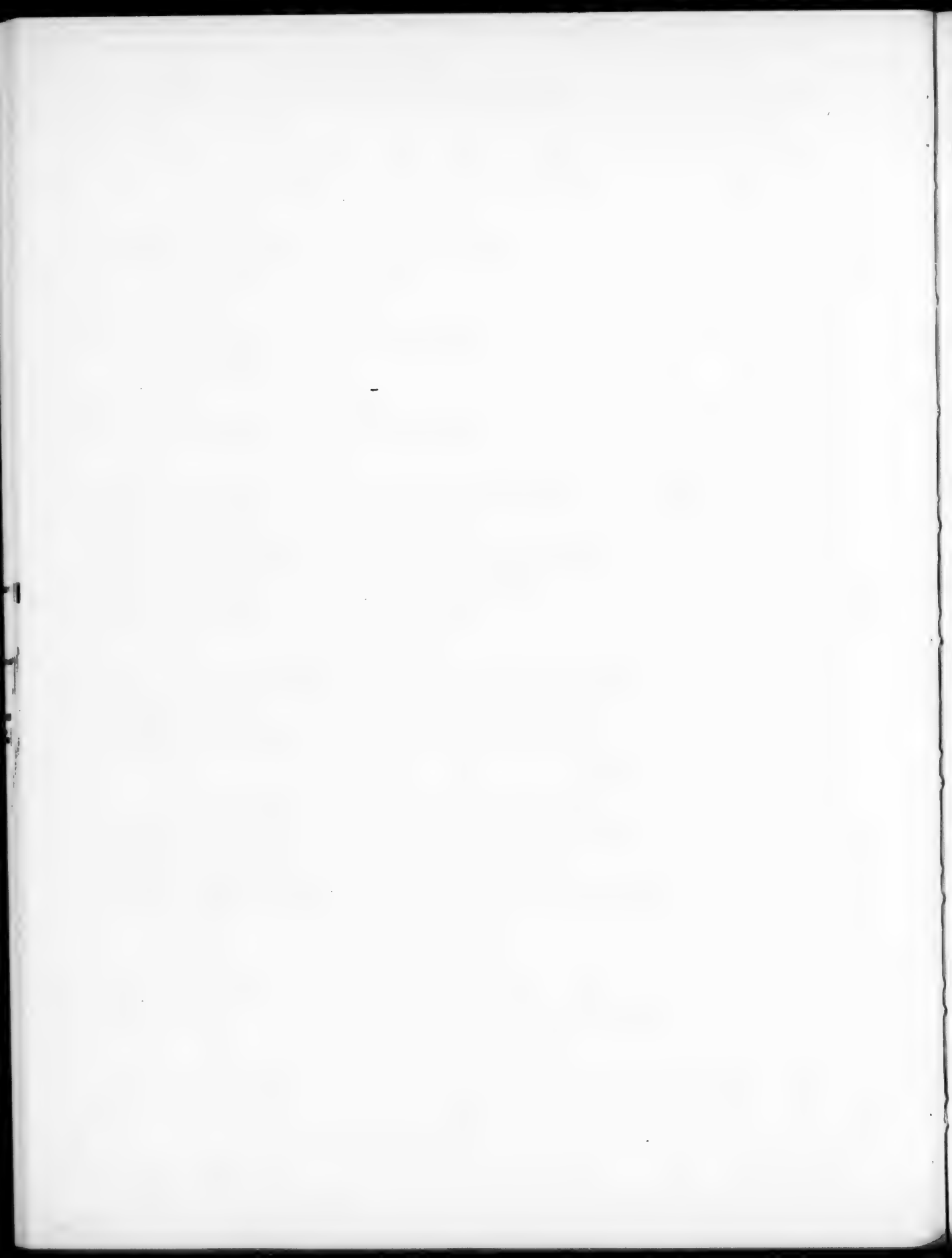
The alcoholic filtrate (after separation of the triarylantimony dichloride) was poured into cooled 5% ammonia solution. The gelatinous precipitate of diarylstibinic acid was filtered off, well washed with water and dried in the air. The acid was identified by conversion to diarylantimony trichloride by heating with 5N hydrochloric acid.

SUMMARY

1. A method was developed for synthesis of previously unknown double diazonium salts of antimony pentachloride.
2. A method was evolved for synthesis of organoantimony compounds of the type of Ar_2SbX_3 and Ar_3SbX_2 via the double diazonium salts of antimony pentachloride.

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BROMINATION WITH DIOXANE DIBROMIDE
III. BROMINATION OF AROMATIC HYDROCARBONS AND HETEROCYCLES.

A NEW METHOD OF IODINATION WITH THE HELP OF THE
COMPLEX OF IODINE CHLORIDE WITH DIOXANE

A. P. Terentyev, L. I. Belenky and L. A. Yanovskaya

In the preceding papers [1, 2] we submitted the results of our work on the application of the dioxane dibromide complex to the bromination of polyhydric phenols and aliphatic aldehydes and ketones. In the present paper we report on the utilization of dioxane dibromide for bromination of aromatic hydrocarbons and some heterocyclic compounds; we also described a series of experiments with aromatic amines *.

In addition we present some results on the application of a new iodinating agent - the complex of iodine chloride with dioxane.

1. Bromination of aromatic hydrocarbons and heterocycles with dioxane dibromide

We tested the action of dioxane dibromide on benzene, toluene, naphthalene, 2-methylnaphthalene, fluorene and anthracene. It was found that benzene does not react with dioxane dibromide either at room temperature or on boiling. Toluene readily enters into reaction with dioxane dibromide on heating to 35-40° and forms *p*-bromotoluene in quantitative yield. Naphthalene and 2-methylnaphthalene react with dioxane dibromide even at room temperature to give the corresponding monobromo derivatives in good yield. When using a twofold excess of dioxane dibromide, naphthalene gives 1,4-dibromonaphthalene. In all cases the reaction was carried out without a solvent. Fluorene reacts in a similar way to naphthalene, forming 2-bromofluorene or 2,7-dibromofluorene depending upon the amount of reactant. The reaction of dioxane dibromide with anthracene proceeds in two ways: In presence of even the slightest trace of moisture, anthrone and anthraquinone are formed. A similar observation was earlier made by Price and Weaker [3] who brominated anthracene in dioxane with bromine. In this case the reaction undoubtedly proceeded via intermediate formation of dioxane dibromide. In absolute dioxane the bromination of anthracene proceeds at 70° and leads to 9-bromoanthracene or 9,10-dibromoanthracene depending upon the ratio of reactants.

With the objective of developing a method of bromination of acidophobic heterocyclic compounds, we tried the action of dioxane dibromide on a series of compounds of the furan and pyrrole series and also on thiophene. Furan itself in small amounts (upto 5 g) is smoothly brominated by dioxane dibromide in ether or dioxane at 0° with formation of 2-bromofuran. When using large amounts of furan, however, the reaction proceeds differently, apparently with opening of the furan ring. After the reaction mixture had been worked up with water, the ether layer did not contain any other substances apart from a negligible amount of dioxane, i.e. the reaction products are water-soluble and pass into the water on washing. Treatment under anhydrous conditions (neutralization of the mixture with sodium carbonate followed by filtration) leads to separation (after removal of the ether) of a dark oil with a pungent odor which does not distil without decomposition. Sylvan is smoothly brominated by dioxane dibromide but the resultant bromosylvan is unstable and after removal of the solvent it violently and spontaneously decomposes. Judging by the outward appearance (a heavy oil with a pleasant odor) bromosylvan contains bromine in the nucleus and not in the side chain. According to the literature, 2-bromomethylsylvan is likewise unstable, but it possesses strong lachrymatory properties which were not found in our case. Furfuryl alcohol, furfural, and furfural diacetate apparently also undergo fission by dioxane dibromide, only water-soluble products being obtained.

Pyrrole and 2,4-dimethylpyrrole are resinified on bromination with dioxane dibromide. On the other hand, 2-acetylpyrrole, 2,5-dimethyl-3-carbethoxypyrrole, 2,4-dimethyl-3-carbethoxypyrrole and 2,4-dimethyl-5-carbethoxypyrrole form the monobromo-derivatives in excellent yields. Also successfully brominated are indole to 3-bromoindole and 2-methylindole to 3-bromo-2-methylindole. 3-Methylindole enters into reaction with dioxane dibromide (decolorization of the reaction mixture), but the bromination product is unstable and decomposes in the course of

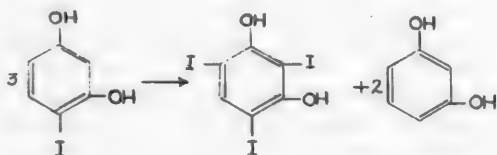
* A paper was recently published by G. M. Kosolapoff on "Direct halogenation of some aromatic amines" [J. Am. Chem. Soc., 75, 3596 (1953)]. The author mentions that complexes of dioxane with halogens can serve as mild agents for halogenation of sensitive aromatic compounds. Examples were given of the preparation of some bromo-substituted aromatic amines. The author does not cite our work on the application of dioxane dibromide although the first communication by one of us was published in 1950 (Proc. Acad. Sci. USSR, 71 693) and was abstracted in the same year in Chem. Abs., 44, 8354 (1950) (abstractor G. M. Kosolapoff).

1-2 hours after preparation. For this reason we were unable to obtain satisfactory analytical results for bromoskatole. Thiophene is brominated by dioxane dibromide to 2-bromothiophene. In all cases the bromination of heterocyclic compounds in ether or dioxane is effected at 0° or at room temperature.

Bromination of aniline or dimethylaniline under our usual conditions, i.e. in ether or dioxane solution, did not proceed smoothly: the reaction mixture turned blue and a dark precipitate appeared. The reaction proceeds differently in acetic acid. For example, on brominating dimethylaniline with dioxane dibromide in acetic acid, a good yield of p-bromodimethylaniline is obtained. Results of the reaction with aniline are also worse. With a twofold excess of dioxane dibromide, however, we succeeded in obtaining 2,4-dibromoaniline in respectable yield.

2. A new iodinating agent - the complex of dioxane with iodine chloride

None of the existing methods of iodination is really satisfactory for the iodination of acidophobic compounds. In searching for a simple and convenient method of direct iodination of acidophobic compounds, we tried out some complexes of dioxane in the iodination of active aromatic compounds (phenols) and of some accessible substances with heterocyclic structures (indole and 2-methylindole). An attempt to iodinate phenol and β -naphthol with dioxane diiodide, described by A. E. Favorsky [4], was unsuccessful. Reaction likewise failed to take place between β -naphthol and the complex of dioxane with iodine bromide [5]. Finally we employed the complex of iodine chloride with dioxane for the purpose of iodination. This substance with the composition $C_4H_8O_2 \cdot ICl$ forms beautiful orange crystals [5] with m.p. 55-58°, readily soluble in organic solvents. In water and on standing in the air, dioxane-iodine chloride gradually decomposes. We did not isolate this reagent in the free state but prepared it immediately before reaction by mixing dioxane with iodine chloride. The procedure for iodination did not differ from that for bromination with dioxane dibromide. With the help of dioxane-iodine chloride, iodinations were effected of phenol, β -naphthol and salicylic acid and the monoiodo-derivatives were obtained in high yields. Iodination of resorcinol by the usual procedure leads to triiodoresorcinol, but in presence of sodium bicarbonate we succeeded in obtaining monoiodoresorcinol. Evidently under the usual conditions the initially formed monoiodoresorcinol disproportionates in presence of hydrogen chloride according to the scheme:



In the literature there is actually reported [6] a similar reaction of monoiodoresorcinol dimethyl ether under the action of a series of reagents including a solution of hydrogen chloride in ether.

In ethereal solution indole is resinified by dioxane-iodine chloride; in pyridine, however, the reaction proceeds smoothly with formation of 3-iodoindole. 2-Methylindole is also successfully iodinated to 3-iodo-2-methylindole. 3-Methylindole does not iodinate under these conditions nor under the action of iodine (when the 3-methylindole is in alkali solution [7]). N- β -Dicyanoethylindole is likewise not iodinated by dioxane-iodochloride.

EXPERIMENTAL

1. Bromination of toluene. To 9.5 g toluene was added dioxane dibromide prepared from 15.1 g bromine and a slight excess of dioxane. At room temperature the reaction does not take place to an appreciable extent. Heating (35-40°) of the reaction mixture caused rapid decolorization and separation of hydrogen bromide. The mixture was run into 10% NaOH solution and the resultant heavy oil was extracted with ether; the ethereal solution was washed with water and dried with calcium chloride. Distillation gave 16.8 g product with b. p. 132-134°; cooling with snow and salt caused the substance to solidify to easily fusible, white crystals with m.p. 26-27° (p-bromotoluene has m.p. 28.5°).

2. Bromination of naphthalene. 6.4 g naphthalene was mixed with crystalline dioxane dibromide prepared from 8 g bromine. The resultant mixture quickly became liquid and then became decolorized. The reaction mixture was washed with water and extracted with ether. The ethereal layer was dried with calcium chloride and fractionally distilled. After redistillation a product was obtained (7.5 g) with b.p. 148-150° (22 mm), n_D^{20} 1.6574, which agrees with the constants of 1-bromonaphthalene.

3. Bromination of 2-methylnaphthalene. 7.1 g 2-methylnaphthalene was brominated with dioxane dibromide, prepared from 8 g bromine, as described above. 8.8 g substance was isolated with b.p. 164-165° (16 mm), 139-140° (7 mm) n_D^{20} 1.6496, corresponding to 1-bromo-2-methylnaphthalene.

4. Bromination of fluorene. From 1.66 g fluorene and 2.5 g dioxane dibromide was obtained (after pouring the reaction mixture into water) 2.45 g 2-bromofluorene with m. p. 110-111° (from alcohol).

Employment of a twofold excess of dioxane dibromide and moderate heating (40-50°) of the reaction mixture to induce decolorization gave 2,7-dibromofluorene in quantitative yield with m.p. 165-166° (from alcohol).

5. Bromination of anthracene. 1.78 g anthracene was brominated in anhydrous dioxane with dioxane dibromide prepared from 0.6 ml bromine, by heating to 65-70° on a water bath. After decolorization, the mixture was poured into water and the crystals were recrystallized from alcohol; the melting point of the yellow crystals was 99-99.5°, corresponding to 9-bromoanthracene. The yield of the recrystallized product was quantitative.

Employment of a twofold excess of dioxane dibromide under the same conditions gave a quantitative yield of 9,10-dibromoanthracene with m.p. 224-225° (from xylene).

6. Bromination of furan. 4.2 g furan was brominated in dioxane solution, while cooling with snow, by gradual addition of a solution of 16 g dioxane dibromide in dioxane. The resultant transparent solution was poured into a solution of sodium carbonate and the oil which separated was steam-distilled. The distillate was extracted with ether. The ethereal extract was dried with anhydrous magnesium sulfate and carefully fractionated. Yield 7 g 2-bromofuran with b.p. 103-104° and n_D^{20} 1.4980, in agreement with the literature data.

7. Bromination of sylvan. 16.4 g sylvan was brominated with 50 g dioxane dibromide in ether-dioxane solution at 0°. The solution was thoroughly washed with water, alkali and again with water, and dried with anhydrous magnesium sulfate; the ether was cautiously distilled off. The residue contained a heavy oil with a pleasant odor which in 15-20 minutes suddenly and violently decomposed with evolution of hydrogen bromide and formation of a black resin. All attempts to isolate the oil in the pure state, apply steam distillation, were unsuccessful; on heating, the oil instantaneously decomposed.

8. Bromination of indole. 0.59 g indole was brominated in ether solution at 0° by addition in small portions of a solution of dioxane dibromide (from 0.256 ml bromine) in ether. The reaction mixture was washed with sodium bicarbonate solution, and with water and dried with anhydrous sodium sulfate. After evaporation of the ether, a residue of silver white leaflets of 3-bromoindole was obtained; m.p. 67° (with decomp.) from ligroine. The leaflets quickly darkened when kept. Yield 0.59 g (60% of the original indole).

9. Bromination of 2-methylindole. 1.31 g 2-methylindole was brominated with 2.5 g dioxane dibromide in a similar manner to indole to give 1.68 g 3-bromo-2-methylindole with m.p. 86-87° (from ligroine); a mixed test with a sample of 3-bromo-2-methylindole prepared by bromination of 2-methylindole with chloramine T and potassium bromide [8] did not give a depression.

10. Bromination of 3-methylindole. 0.65 g 3-methylindole was brominated with 1.25 g dioxane dibromide in the same manner as indole. Evaporation of the ether from the dried ethereal layer left 0.70 g crystalline product with m.p. 77° (with decomp. from ligroine). After keeping for a short period (1-2 hours), however, the product darkened and decomposed. We were consequently unable to obtain precise analytical data: the C, H and Br contents of the product varied sharply in the course of analyses of a single sample. From the results of the first determination the bromine content is about 40%; the composition is close to that of a monobromo- derivative (bromine content 38.6%).

11. Bromination of 2,5-dimethyl-3-carbethoxypyrrole. To 1.67 g 2,5-dimethyl-3-carbethoxypyrrole in 15 ml dioxane was introduced little by little 2.5 g dioxane dibromide at room temperature. The color changed to brownish-violet. The reaction mixture was poured into water, and the precipitate was collected, washed with water and recrystallized from aqueous alcohol. Yield 2.4 g with m.p. 130° (on rapid heating); on slow heating the product decomposes and blackens at 104°.

4.110 mg sub.: 6.625 mg CO₂; 1.850 mg H₂O; 1.335 mg Br. 5.400 mg sub.: 8.710 mg CO₂; 2.450 mg H₂O; 1.755 mg Br. Found %: C 43.99, 44.03; H 5.04, 5.08; Br 32.48, 32.50. C₉H₁₂O₂NBr. Calculated %: C 44.10 H 4.94 Br 32.61.

2,5-Dimethyl-3-carbethoxy-4-bromopyrrole was here prepared for the first time.

12. Bromination of 2-acetylpyrrole. 3.6 g 2-acetylpyrrole was brominated in 30 ml dioxane at room temperature with 9.5 g dioxane dibromide. The mixture was poured into water and the precipitate filtered and dried to give 3.5 g bromo-2-acetylpyrrole with m.p. 108° (with decomp.).

9.025 mg sub.: 0.552 ml N₂ (21°, 761 mm). 5.465 mg sub.: 0.340 ml N₂ (21°, 761 mm). Found %: N 7.11, 7.23. C₆H₆ONBr. Calculated %: N 7.45. 5.575 mg sub.: 7.853 mg CO₂; 1.580 mg H₂O; 2.404 mg Br. 4.270 mg sub.:

6.027 mg CO₂; 1.290 mg H₂O; 1.825 mg Br. Found %: C 38.44, 38.52 H 3.17, 3.30; Br 43.01, 42.72. C₆H₆ONBr. Calculated %: C 38.33; H 3.22; Br. 42.51.

We did not establish the structure of bromo-2-acetylpyrrole.

13. Bromination of 2,4-dimethyl-3-carbethoxypyrrole. Bromination with 2.5 g dioxane dibromide in dioxane at room temperature gave 5-bromo-2,4-dimethyl-3-carbethoxy pyrrole. Yield 95%, m.p. 96° (from alcohol).

14. Bromination of 2,4-dimethyl-5-carbethoxypyrrole. Procedure as before. A quantitative yield of 3-bromo-2,4-dimethyl-5-carbethoxypyrrole was obtained; m.p. 150-151° (from alcohol).

15. Bromination of thiophene. 3.36 g thiophene was brominated in ether solution with 7.5 g dioxane dibromide while stirring and cooling with water; after working up as usual, fractionation gave 6.5 g 2-bromothiophene with b.p. 43-44° (15 mm), n_D^{20} 1.5868.

16. Bromination of acetanilide. To a solution of 1.35 g acetanilide in dioxane was added 2.5 g dioxane dibromide. The mixture quickly decolorized. After pouring into water, 2.1 g p-bromoacetanilide was obtained with m.p. 167-168° (from alcohol).

17. Bromination of N,N-dimethylaniline. To a solution of 12.1 g N,N-dimethylaniline in acetic acid was added 25 g dioxane dibromide in 1-2 g portions with shaking; the solution quickly decolorized. The mixture was run into a large volume of dilute alkali and an oil separated out which soon crystallized after treatment with water. Yield 2 g 4-bromo-N,N-dimethylaniline. m.p. 55-56° (from aqueous alcohol).

18. Bromination of aniline. To a solution of 9.3 aniline in acetic acid was added 50 g dioxane dibromide in the manner described above. The darkened solution was run into dilute alkali. The precipitate was collected, washed with water and recrystallized from aqueous alcohol. Yield 14.5 g product with m.p. 79-80° (2,4-dibromoaniline).

19. Iodination of phenol. To a solution of 3 g phenol in 30 ml carbon tetrachloride was gradually added a mixture of 4.9 g iodine chloride and 5 ml dioxane. After 1 1/2 hours the mixture was washed with sodium carbonate solution and dried with fused potassium carbonate. The oil remaining after evaporation of the solvent crystallized on rubbing in presence of water. Yield 5.1 g moniodophenol (mixture of o- and p-isomers). Pure p-iodophenol with m.p. 93° was isolated by fractional precipitation with carbon dioxide gas from a solution of the iodophenol in 10% NaOH.

20. Iodination of salicylic acid. To a solution of 1.8 g salicylic acid in 5 ml dioxane was added with stirring a solution of 2.1 g iodine chloride in 3 ml dioxane. The next day the mixture was poured into sodium sulfate and 3 g 5-iodosalicylic acid was obtained with m.p. 192° (from aqueous alcohol).

21. Iodination of β -naphthol. To a solution of 1.4 g β -naphthol in 5 ml ether was added a mixture of 1.5 g iodine chloride and 2 ml dioxane. Working up in the usual way gave 2.4 g 1-iodo-2-naphthol with m.p. 94.5° (from dilute alcohol).

22. Iodination of resorcinol. To 1.65 g resorcinol in 20 ml ether was added a solution of 2.4 g iodine chloride in 5 ml dioxane and 10 ml ether. Working up was carried out as usual after 1 hour. Evaporation of the ether left a poorly crystallizing oil which crystallized after treatment with water and standing. Yield 1.2 g 2,4,6-triiodoresorcinol with m.p. 144°.

1.3 g resorcinol was iodinated in 20 ml ether in presence of 2 g sodium bicarbonate powder with a mixture of 1.5 g iodine chloride and 5 ml dioxane. The usual treatment followed by evaporation of the ether gave 2.15 g oil which slowly (in the course of several weeks) crystallized. The crystals had m.p. 60°; after standing in the air the melting point rose to 93°. Due to the high solubility of the substance in water and organic solvents, it could not be recrystallized. According to the literature, 4-iodoresorcinol crystallizes with one molecule of water and the monohydrate has m.p. 63°; on standing in the air the water is lost; the melting point of the anhydrous preparation is 100° [9].

23. Iodination of indole. To a solution of 0.6 g indole in 5 ml pyridine was added, with stirring and snow cooling, a mixture of 0.85 g iodine chloride and 5 ml dioxane. The resultant solution was poured into water and extracted with ether. Evaporation of the ether left 1.2 g 3-iodoindole with m.p. 75° (with decomp.; from ligroine).

24. Iodination of 2-methylindole. 0.5 g 2-methylindole was iodinated with a mixture of 0.65 g iodine chloride and 5 ml dioxane under the conditions of iodination of indole. Yield 0.65 g 3-iodo-2-methylindole with m.p. 81.5° (from ligroine).

SUMMARY

1. Dioxane dibromide is a mild brominating agent for a series of aromatic hydrocarbons and amines, thiophene, and some derivatives of pyrrole and indole.

2. A new method of iodination is proposed with the help of the dioxane-iodine chloride complex and is applied to phenols and some indoles.

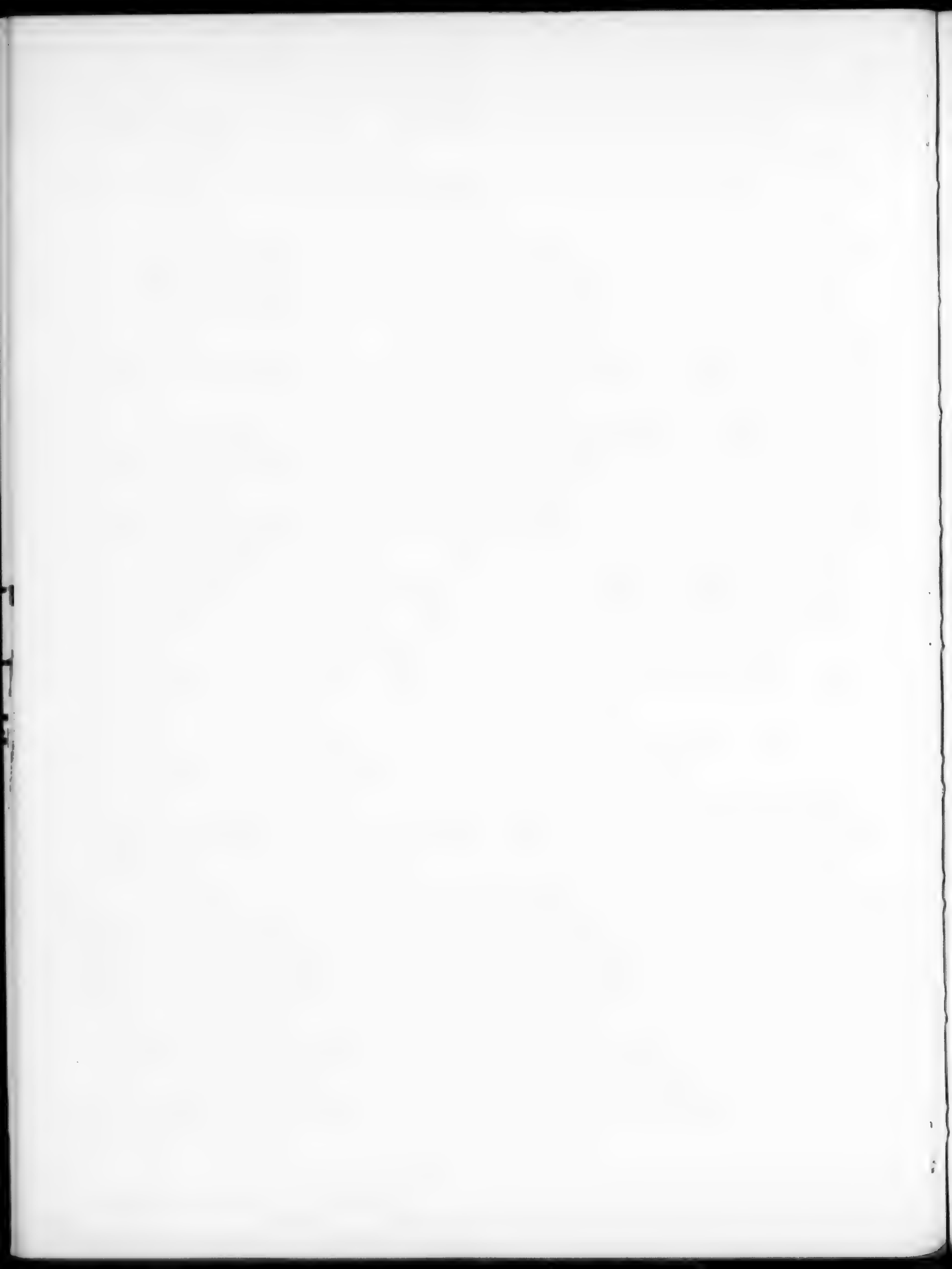
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Received January 28, 1954

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* T.p. = C. B. Translation pagination.



THE STRUCTURE OF PALUSTROL

N. P. Kiryalov

Palustrol, a saturated tertiary tricyclic alcohol of the composition $C_{15}H_{26}O$ was first [1] isolated from the essential oil of the marsh rosemary (*Ledum palustre* L.).

Not long ago investigations [1, 2] showed that palustrol belongs to the group of azulene-forming sesquiterpene alcohols since on heating with dehydrogenating agents (S, Se, Pd) palustrol readily forms a blue liquid containing 1,4-dimethyl-7-isopropylazulene (picrate with m.p. 121-122°).

It is also important to note that on heating with acids (H_2SO_4 , HCl, HCOOH) palustrol is dehydrated with facility to form bicyclic or tricyclic hydrocarbons with the formula $C_{15}H_{24}$, which justifies the assumption that palustrol belongs to the group of tertiary tricyclic alcohols. As the investigations showed [1, 2], under mild dehydration conditions palustrol splits off water with formation of tricyclic hydrocarbons containing one double bond, while under more drastic conditions dehydration leads to more far-reaching modification involving scission of the cyclopropane ring (the presence of a cyclopropane ring was demonstrated by physical methods and by the reactions of the compound) and formation of bicyclic hydrocarbons with two double bonds.

On comparing the above-mentioned results of investigation of palustrol with what is known about the chemical properties of ledol [3, 4], we see that palustrol and ledol are almost identical in their behavior toward acids or dehydrogenating agents, and that they form very similar or identical products of reaction. These facts suggest a similarity of structure of both these compounds, although palustrol and ledol possess different physical properties (Table 1).

TABLE 1

Compound	Formula	Boiling point	n_D^{20}	Melting point	Odor
Palustrol	$C_{15}H_{26}O$	276-278°	-17°	Liquid	Musty odor
Ledol	$C_{15}H_{26}O$	282-283°	+5°	105-106.5°	Nearly odorless

The results of a further study of palustrol described in the present paper confirm the similarity between the structures of palustrol and ledol. This facilitates the elucidation of the structure of palustrol since that of ledol is already known [4] and corresponds to structural formula (I).

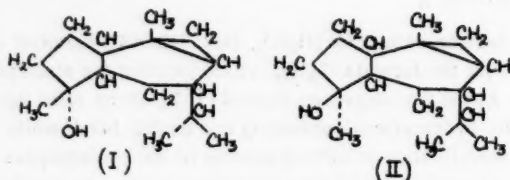
Palustrol was isolated from marsh rosemary oil and dehydrated, and the resultant tricyclic hydrocarbons, palustrenes [probable structures (III) and (IV)], were oxidized. Oxidation gave two crystalline substances - ledic acid $C_{15}H_{24}O_3$ [m.p. 155-156°; probable structure (V)] and ledglycol $C_{15}H_{26}O_2$ [m.p. 151-152°; probable structure (VI)]. These derivatives were previously found, as reported [3, 4], among the products of oxidation of ledene. The yield of ledglycol and ledic acid on oxidation of the mixture of palustrenes, however, differs considerably from the yield of these compounds after oxidation of the mixture of ledenes. Thus the oxidation of a mixture of ledenes gave 40-50% ledglycol and 1-2% ledic acid, whereas oxidation of the mixture of palustrenes gave only 20-30% ledglycol (or in the most favorable case 25%) and 7-10% ledic acid. It should be observed that the low yield of ledglycol on oxidation of palustrenes may be explained to a certain extent by the fact that 15-20% of the ledglycol could not be crystallized from the products of oxidation. The presence of ledglycol in the mother liquor of the oxidation products could be inferred from our isolation from the mother liquor of an unsaturated ketone - $\Delta^{5,6}$ -2,5-dimethyl-8-isopropyl-1-octalone (VIII) - the product of dehydration of ledglycol in an acidic medium which is accompanied by rearrangement [4].

Originally we suggested that specimens of palustrol at our disposal and used for the investigation (Table 2) contain a considerable amount of ledol as impurity (of the order of, say, 50%), since only a very high content of ledol in palustrol could entitle us to say that the results of oxidation of palustrenes were not determined by the structure of palustrol. To verify this hypothesis, various samples of palustrol (Table 2) were subjected to cooling (to -60°) and to fractional distillation. Neither method gave indication of the presence of considerable amounts of ledol in the investigated samples of palustrol. The presence of traces or even small amounts (up to 1-2%) ledol in the sample of palustrol is certainly possible. The separation of the impurities by physical methods, however, was extremely difficult

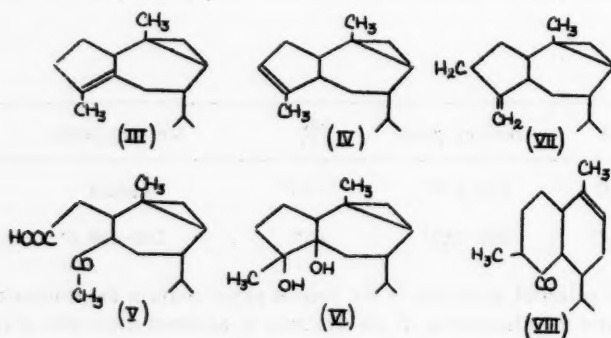
and was not of material importance for the present investigation. It was important to establish that the main products of oxidation of palustrenes (from palustrol) were identical with the products of oxidation of ledenes (from ledol).

Bearing in mind that dehydration of palustrol was performed under conditions similar to those of dehydration of ledol and that no double bond translocations were observed on distillation of palustrenes (palustrenes form identical crystalline products before and after distillation, i. e. ledic acid and ledglycol), it is reasonable to assume that the hydroxyl group of ledol and palustrol is attached to the same carbon atom. Palustrol consequently differs from ledol in that palustrol is either a levorotatory optical isomer of ledol or a levorotatory diastereomer of ledol. We hold to the view that palustrol is a levorotatory diastereomer of ledol because the rotatory power of ledol is $[\alpha]_D +5^\circ$; $\alpha_D +5^\circ$ ($c = 10$; in alcohol), whereas palustrol has $\alpha_D -17^\circ (\pm 0.4^\circ)$.

On the assumption that ledol has structure (I), we may suggest structure (II) for palustrol; this differs from (I) only in the spatial position of the hydroxyl group.



On the basis of structure (II) we may suggest that dehydration of palustrol gives mainly α - and β -palustrenes [probable structures (III) and (IV)]; γ -palustrene [possible structure (VII)] is not formed. Oxidation of β -palustrene gives ledic acid (V), while α -palustrene gives ledglycol (VI).



The possibility of formation of hydrocarbons (III) and (IV), and also of compounds (V) and (VI) has already been indicated [3, 4].

On the basis of a comparison of the structural formulas of α - and β -palustrenes with those of α - and β -ledenes [4] we may conclude that they are identical and that the names of the hydrocarbons are synonymous. This conclusion is obviously correct because ledglycol and ledic acid prepared by oxidation of ledenes or palustrenes possess the same sign and magnitude of rotation.

TABLE 2

Properties of the palustrol used in the investigation

Specimen number	d_{20}^{20}	n_D^{20}	α_D	Boiling point	Percent alcohol by the Chugaev-Zerewitinov method
1	0.9593	1.4911	$-16.9^\circ (18^\circ)$	123-126° (2 mm)	99.4
2	0.9615	1.4914	$-16.5^\circ (18^\circ)$	128-131 (3 mm)	99.6
3	0.9588	1.4917	$-16.65^\circ (21^\circ)$	127-131 (2-3 mm)	96.87
4	0.9643	1.4916	$-17.1^\circ (25.5^\circ)$	130-132 (3 mm)	101.2
5	0.9593	1.4908	$-17.35^\circ (20^\circ)$	127-131 (3 mm)	99.0

EXPERIMENTAL

Specimens of palustrol (Table 2) were obtained from marsh rosemary oil by the previously described procedure [2].

Palustrol was additionally characterized by the determination of its Raman spectrum. A ISP-51 spectrograph was used; the light source was a quartz-mercury lamp (excited by the λ 4358.3 Å line); width of slit 0.007 mm; period of exposure 3 hours.

The Raman spectrum of palustrol contains the following lines ($\Delta \nu$ in cm^{-1}): 261 (5), 295 (1), 332 (2), 444 (10), 475 (2), 508 (2), 636 (1), 706 (10), 757 (5), 790 (10), 827 (2), 870 (4), 977 (10), 1094 (1), 1242 (5), 1304 (1), 1342 (1), 1441-1454 (10). *

Behavior of palustrol at low temperatures

1. On cooling to -60° palustrol is transformed into a vitreous mass which becomes liquid at -40° .
2. An alcohol solution (1:3) of palustrol changes into a slurry at -55° but again forms a transparent solution at -43° . Ledol does not separate on rapid filtration at the pump at low temperatures. Introduction into a cooled solution of palustrol of a small crystal of ledol does not cause crystallization and the crystal remains undissolved.
3. 1 g ledol and 2 g palustrol were dissolved in 5 ml 80% ethyl alcohol and the solution was cooled to -15° ; the ledol (1 g) separated unchanged.

Dehydration of palustrol

40 g palustrol was dissolved in 80 ml 96% alcohol and run into a solution of 4 ml sulfuric acid in 8 ml alcohol. The mixture was heated to the boil; when the liquid had become cloudy, gentle heating was maintained for eight minutes. The upper oily layer (40 ml) was separated, washed with water, dried with sodium sulfate and distilled at 5-6 mm over Na. Two fractions were obtained: 1st - b.p. up to 130° , 29 g; 2nd - b.p. $130-135^\circ$, 5.3 g. The first fraction was redistilled over Na to give a colorless oil with b.p. $112-115^\circ$ (5 mm). Yield about 25 g.

n_D^{20} 1.4978, d_4^{20} 0.9207

Found %: C 88.06; H 11.72. $\text{C}_{15}\text{H}_{24}$. Calculated %: C 88.16; H 11.84.

In properties the oil closely resembles the hydrocarbon palustrene [2].

Dehydrogenation of palustrene

3 g palustrene and 2 g selenium were heated to $240-255^\circ$ for 3 hours. The mixture quickly became violet. The oil was distilled with steam and dissolved in low-boiling gasoline and the azulene was extracted with 90% phosphoric acid. The phosphoric acid extract was diluted with water and the separated oil was extracted with ethyl ether. The ethereal solution was dried with sodium sulfate and the ether distilled off. The residue was a violet oil, weight about 0.2 g. To this oil was added a saturated alcoholic solution of picric acid (0.2 g). A picrate was obtained in the form of dark needles with m.p. $121-122^\circ$ (after three recrystallizations from alcohol). The picrate did not give a depression in a mixed test with the picrate of 1,4-dimethyl-7-isopropylazulene. The picrate of the product of dehydrogenation of ledene is known to have m.p. $122-123^\circ$ and does not differ from the picrate of 1,4-dimethyl-isopropylazulene [4]. The previously prepared [2] picrate with m.p. $118-119^\circ$ was evidently insufficiently pure.

Oxidation of palustrene

20 g palustrene was dissolved in 700 ml acetone and to the solution was gradually added a solution of potassium permanganate (30 g KMnO_4 in 300 ml water). After decolorization of the solution, the manganese dioxide was filtered off and washed with acetone and hot water. The acetone was distilled off, the supernatant oily layer was collected and the aqueous layer was extracted with ether. Acidification of the aqueous solution gave a voluminous precipitate. M.p. $155-156^\circ$ (from aqueous alcohol); $[\alpha]_D^{20} + 127^\circ$. The substance did not give a depression in a mixed melting test with ledic acid of the composition $\text{C}_{15}\text{H}_{24}\text{O}_3$, prepared by oxidation of ledene [3]. Yield 1.4-2 g (i.e. up to 10% of the original hydrocarbon).

Found %: C 71.44; H 9.55. $\text{C}_{15}\text{H}_{24}\text{O}_3$. Calculated %: C 71.39; H 9.58.

The ethereal solution was dried with sodium sulfate and the ether was distilled off to leave a partly crystallizing oil. The crystalline portion had m.p. $151-152^\circ$ (from gasoline); $[\alpha]_D -18.2^\circ$ ($c = 5$; in alcohol). The product did not give a depression of melting point in admixture with a pure preparation of ledglycol [3]. Yield 4g (approx. 20%).

Found %: C 75.52; H 11.08. $\text{C}_{15}\text{H}_{26}\text{O}_2$. Calculated %: C 75.58; H 10.99.

In addition to ledic acid and ledglycol, 14.85 g liquid products of oxidation was obtained. From the liquid portion 4 ml volatiles was distilled off with steam. Into the residue of non-steam-distillable oxidation products was run

* The figures in brackets refer to the intensities of the lines as visually evaluated.

sulfuric acid in such quantity that the solution had 2% concentration; the steam distillation was then resumed. About 4 ml dark-red liquid was collected. B.p. 130-145° (3 mm), n_D^{24} 1.5080, d_{20}^{20} 0.9742. The liquid was crude $\Delta^{5,6}$ -2,5-dimethyl-8-isopropyl-1-octalone (VIII), as was confirmed by the following two reactions.

1. 1 g substance in admixture with 1 g selenium was heated to the boil (260-280°) for 4 hours. A substance was obtained with $n_D^{18.5}$ 1.532 and forming a picrate with m.p. 130-131° (from alcohol). The picrate did not give a depression in a mixed melting test with the picrate of the unsaturated 2,5-dimethyl-8-isopropyl-1-tetralone [4].

2. Oxidation of 3 g of the oil, dissolved in 150 ml acetone, with potassium permanganate (3 g $KMnO_4$ in 50 ml water) gave 2.5 g neutral (partially crystallizing) products of oxidation containing about 0.6 g pure substance with m.p. 180-182° (from gasoline). This substance did not give a depression in a mixed melting test with the known ketoglycol with the formula $C_{15}H_{26}O_3$ (m.p. 183-185°) previously prepared by oxidation of $\Delta^{5,6}$ -2,5-dimethyl-8-isopropyl-1-octalone.

SUMMARY

Evidence is adduced to show that palustrol is the levorotatory diastereomer of ledol.

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Received October 1, 1953

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* T.p. = C.B. Translation pagination.

